

Near Net-shape Fabrication of Ultrafine Scale Piezoelectric Ceramic/Polymer Composites

Annual Report: March 1995

Contract Number N00014-92-C-0212

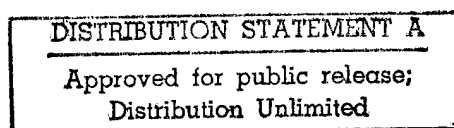


Contractor: Materials Systems Inc., Concord, Massachusetts

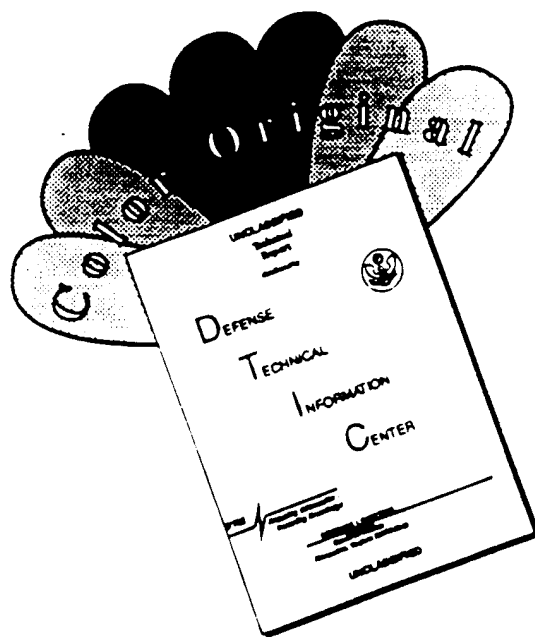
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Near-net Shape Fabrication of Ultrafine Scale Piezoelectric Ceramic/Polymer Composites

Executive Summary

Over the past two years, Materials Systems Inc. (MSI) has demonstrated that net-shape ceramic injection molding is capable of fabricating extremely fine scale 1-3 and 2-2 piezoelectric ceramic/polymer composites for Navy and commercial applications. In its last report (1), Materials Systems described modifications to its injection molding process that allow net shape forming of 1-3 piezocomposite transducer preforms having $<100\mu\text{m}$ wide PZT elements, and outlined several approaches for further developing the process.

Using these approaches, MSI has extended the injection molding capability to include ultrafine scale 2-2 composites having element widths as low as $22\mu\text{m}$, and has continued refining the process and tooling to achieve larger area 1-3 composites, up to 30mm square. The past twelve months have also seen 1-3 piezocomposites injection molded with high PZT volume fraction (~60-80%). Throughout 1993-94, MSI pursued commercialization of these materials, supplying test prototypes under customer funding to both private-sector and Navy composite end-users. As a result, the electro-acoustic properties of these fine-scale composites have been characterized not only by MSI, but also as transducers in customer-proprietary applications.

In addition to the ultrafine scale composites work, a major new initiative began in March 1994 into fine scale piezocomposites for undersea acoustic imaging. The applications drivers are Navy mine hunting systems and diver-held sonar. These materials are also expected to find application in the private sector, especially in medical ultrasound. This task is being undertaken as part of a Technical Cooperation Program (TTCP) in conjunction with other organizations in Canada, the UK, and the USA. In particular, MSI is working with a subcontractor, UltraSound Solutions (USS), to demonstrate composite materials configurations that can be used for electronically beam-steered undersea acoustic imaging. A first generation transducer design has been prepared by USS for use in evaluating these materials for this application.

Overall, the program goals in both the ultrafine scale composites and TTCP activities have been met on schedule and within budget. Feedback on applications from Navy and commercial systems end-users has prompted MSI to perform additional exploratory demonstrations of its process for transducers that operate in the 2-4 MHz frequency range. Navy and medical ultrasound interest in this frequency range remains strong, and has been factored into MSI's recommendations to ONR for continuation of this work during 1995-96.

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1. Objective and Deliverables

The program is divided into two major tracks:

Track 1: Ultrafine Scale Piezocomposites

The primary Track 1 objective is to advance the state-of-the-art in near-net shape fabrication of ultrafine scale PZT ceramic/polymer composites. The scope of work includes 2-2 type composites having PZT element dimensions down to 10 μ m. For 1-3 composites the ultimate dimensional goal is 25 μ m fiber diameter. Piezocomposite process scale-up to produce composite pieces 30-50mm square is a key program objective.

In pursuing the Track 1 objectives, MSI has focussed on forming processes that are expected to be capable, after scale-up, of economically manufacturing ultrafine scale piezoelectric composites for both Navy and commercial applications, such as medical ultrasonic imaging.

Figure 1 shows the Track 1 tasks and timing.

Track 2: TTCP Piezocomposites

The TTCP activity, aimed at evaluating piezocomposite transducer materials for several Navy applications, has the following objectives:

Hydrophones: To collaborate with TTCP partners to better understand, through modelling, transducer fabrication, and testing, how 1-3 piezocomposites improve the performance of hydrophones for flank arrays and other applications.

Multilayer 1-3 transducers: In collaboration with TTCP partners, to develop techniques for fabricating double layer and multilayer 1-3 composite transducers for undersea sensing and actuation.

Piezocomposites for Undersea Imaging: To demonstrate a prototype electronically beam-steered piezocomposite array for use in mine hunting.

In Track 2, the primary role performed by MSI is to provide composite transducer materials and devices, and to develop techniques for fabricating new piezocomposite transducer configurations for evaluation within the TTCP. Figure 2 shows the Track 2 tasks and timing.

Deliverables for both tracks include progress reports as required by ONR, and state-of-development demonstration specimens.

| Task | Date | | | | | | |
|--|------|-------|------|------|------|-------|------|
| | 9/93 | 12/93 | 3/94 | 6/94 | 9/94 | 12/94 | 3/95 |
| Task 1: Molding Equipment | | | | | | | |
| - Separate Designs for Molder and Ejector. | | | | | | | |
| - Consolidated Design. | | | | | | | |
| Task 2: Tool Insert Fabrication | | | | | | | |
| - Design and Order Tool Inserts. (Stiffer materials; 1-3; 2-2) | X | X | X | | | | |
| - Larger Inserts. | | | | X | X | | |
| Task 3: Process Research | | | | | | | |
| - 1-3 Composite Arrays. | | | | | | | |
| - 2-2 Composite Arrays. | | | | | | | |
| - Alternative Binders. | | | | | | | |
| Task 4: Characterization | | | | | | | |
| - Receive Impedance Analyzer. | | X | | | | | |
| - 1-3 Composite Array Meas. | | | | | | | |
| - 2-2 Composite Array Meas. | | | | | | | |
| - Arrays to acoustic systems vendors for characterization. | | | | | | | |
| Task 5: Reporting | | | | | | | |
| - Oral Progress Reports. | | | | | | | |
| - Final Report. | | | | | | | X |

Figure 1: Track 1 (Ultrafine scale piezocomposites) schedule.

| Task | Date | | | | |
|--|-------|------|-------|------|-------|
| | 12/93 | 6/94 | 12/94 | 6/95 | 12/95 |
| Task 1: Transducer and Materials Design | | | | | |
| - TTCP Design Reviews | X | X | X | X | X |
| - Design Iterations | X | X | X | X | |
| Task 2: Materials Fabrication and Evaluation | | | | | |
| Task 3: Electronically Beam-steered Transducers | | | | | |
| - Determine Undersea Imaging Requirements | | | | | |
| - Review Candidate Imaging Systems | | | | | |
| - Design Beam-steered Array | | | | | |
| - Fabricate and Evaluate Transducer | | | | | |

Figure 2: Track 2 (TTCP piezocomposites) schedule.

2. Accomplishments versus Objectives

Track 1: Ultrafine Scale Piezocomposites

The 1-3 process has been scaled up to 30mm square pieces for PZT element arrays of 100-150 μ m at 0.25 PZT volume fraction. This has allowed MSI to begin high frequency testing, as well as make samples available for evaluation in the private sector. Large area samples having elements smaller than 50 μ m have not yet been achieved, mainly due to technical difficulties encountered with ejection after molding. Further effort in this area is needed to better understand the ejection behavior. An additional effort, aimed at developing fabrication technology for 1-3 composites having coarser elements in the 200-400 μ m range, has been pursued. The impetus for this work is based on feedback from the acoustic imaging systems user community which indicates that transducers having PZT elements in this size range are needed for defense and commercial undersea applications in the frequency range 2-4MHz.

The 2-2 work has proceeded according to plan. The smallest pitch dimension produced to date is 45 μ m, smaller than has been demonstrated by conventional dicing. There appears to be a substantial market for ultrafine scale 2-2 composite transducers in this size range for use in intravascular and endoscopic ultrasound. Applications include both defense (battlefield medical diagnosis and treatment) and commercial uses, especially where low cost facilitates disposable usage.

Major advances were made in the quality of the 1-3 composites, which resulted in arrays of fine scale elements without the defects described in the 1993-4 report. These were accomplished through process refinement, especially tightening the process parameter ranges, and through improved tool design. For the 2-2 composites, much of the tooling and process improvement resulted from IR&D work aimed at improving the process for commercial customer applications. These processes were then applied under Track 1 of this program to achieve ultrafine scale 2-2 composite dimensions.

Track 2: TTCP Piezocomposites

This task is proceeding according to schedule. MSI has supplied custom 1-3 hydrophones for evaluation by NRL-USRD and DRA. Using low cost tooling technology developed under contract number N00014-C-94-0019 (2), MSI has been able to fabricate 1-3 composites having PZT elements of diamond and triangular-shaped cross-section. These are undergoing evaluation at Strathclyde University to seek improvements in interelement mode suppression. In addition, several new types of double layer 1-3 piezocomposite that have thickness mode resonance frequencies under 100kHz have been developed, including some resonating at as low as 45kHz. These frequencies are applicable for some Navy transmit applications where high power, low profile actuation is important, as well as many undersea fish-finding systems. Work on the electronically beam steered array is proceeding according to schedule, and composite development has begun in anticipation of array fabrication.

3. Results

The basic injection molding technology established by MSI for net-shape forming ultrafine scale piezoelectric ceramic/polymer composites has been developed under both ONR funding (for 1-3 configurations) and in-house funding (for 2-2 connectivities). The technology background has been described in the 1993 annual report; this report documents progress throughout 1994 on both technology tracks.

Track 1: Ultrafine Scale Piezocomposites

In its original proposal, MSI provided details of the injection molding process along with a description of the key technical barriers that must be resolved to demonstrate a viable molding process for ultrafine scale composites. Many of the principal technical barriers that were anticipated originally have been resolved, notably binder bleeding during mold filling and the issues associated with tool insert fabrication. Ejection of the molded parts remains the single most important technical issue to date. This process is now much better understood and several improvements are under development as part of the current effort. Technical efforts aimed at extending the forming process to finer dimensions have been particularly successful for 2-2 composites, where PZT element widths below 25 μ m have been achieved. Some of the research results include:

Molding Process Improvements:

The fabrication processes for both 1-3 and 2-2 composites have been improved considerably. To avoid binder bleeding, the process conditions have been adjusted to increase the PZT-binder mix viscosity. This has necessitated changes in molding procedures aimed at accommodating the more viscous mixes. These changes include higher pressures and lower temperatures, requiring modifications to the molding equipment. In particular, MSI built two experimental molders designed to allow increased molding pressure, improved control over temperature, and larger area devices up to 30mm square. Approximately 150 runs have been completed in this experimental set-up, leading to a greater understanding of the mechanisms of molding and ejection. Using procedures established in prior work (1), several sets of 1-3 tool inserts were made to test the new molding procedures and equipment. 1-3 inserts varied in size from 20 to 40mm square, with cavities designed to produce green PZT elements ranging in size from 50 to 150 μ m. After several experimental iterations of molding temperature, pressure and time, complete tool filling was obtained consistently for all of these configurations. Ejection was then studied as a function of temperature, pressure, binder formulation and binder content.

High quality molded parts were obtained consistently for element sizes over 120 μ m, despite the increased tool area. In most cases the parts were removed with all elements intact. (Note that for a 30mm square tool insert, this amounts to approximately 15,000 elements per part.) Problems of element breakage at the corners of the array described in the 1993-4 report were eliminated by applying the ejection pressure more uniformly so that all elements were stressed equally during ejection. Figure 3 shows such an array. The aspect ratio of the PZT rods can be seen clearly in Figure 4, where an area of rods has been broken off and the rods are lying horizontally. The rods are approximately equal in length, uniformly tapered along the length, with an aspect ratio of about 4-5. For very fine element arrays, 50 μ m in diameter, the yield of intact elements has remained low. Fracture usually occurs at the point where the elements contact the PZT baseplate, indicating that this is the region of maximum stress during ejection (the tooling is chamfered in this area to minimize this stress). Occasionally rods fracture across the thinner portion of the diameter around their mid-point. The presence and location of intact PZT rods (Figure 5) indicate that ejection of this composite configuration is feasible. However, considerable further work is required to improve the array quality and obtain high process yields.

Other improvements have been made in the binder removal procedure. The part cross-sections involved in ultrafine scale composites are extremely small. This greatly alleviates the problems normally associated with binder removal in injection molded ceramics, allowing much faster burnout cycles. Accordingly, the binder removal mechanism has been examined to determine how the various time/temperature stages can be accelerated. A multi-hold cycle involving different heating rates has been established, resulting in a decrease in the binder removal time from several days to under 16 hours.

Several challenges remain with binder removal in high PZT volume fraction composites. Since the elements in these materials are arranged very closely, even small amounts of warpage during binder removal can result in adjacent elements coming into contact and collapsing. The problem is associated with certain composite features, in particular PZT element aspect ratios in excess of ten, and very fine elements less than 50 μ m wide.

1-3 and 2-2 Piezocomposite Scale-up:

The composite dimensions achieved during the earlier portion of the work were limited to molded pieces approximately 10mm square. Over the past year, these have been increased to 30mm square, large enough to enable MSI to begin selling samples of 1-3 composite for customer evaluation. These fabrication procedures are still experimental in terms of piezocomposite manufacturing. However, the original program goal of 30-50mm square composite samples has been largely met.

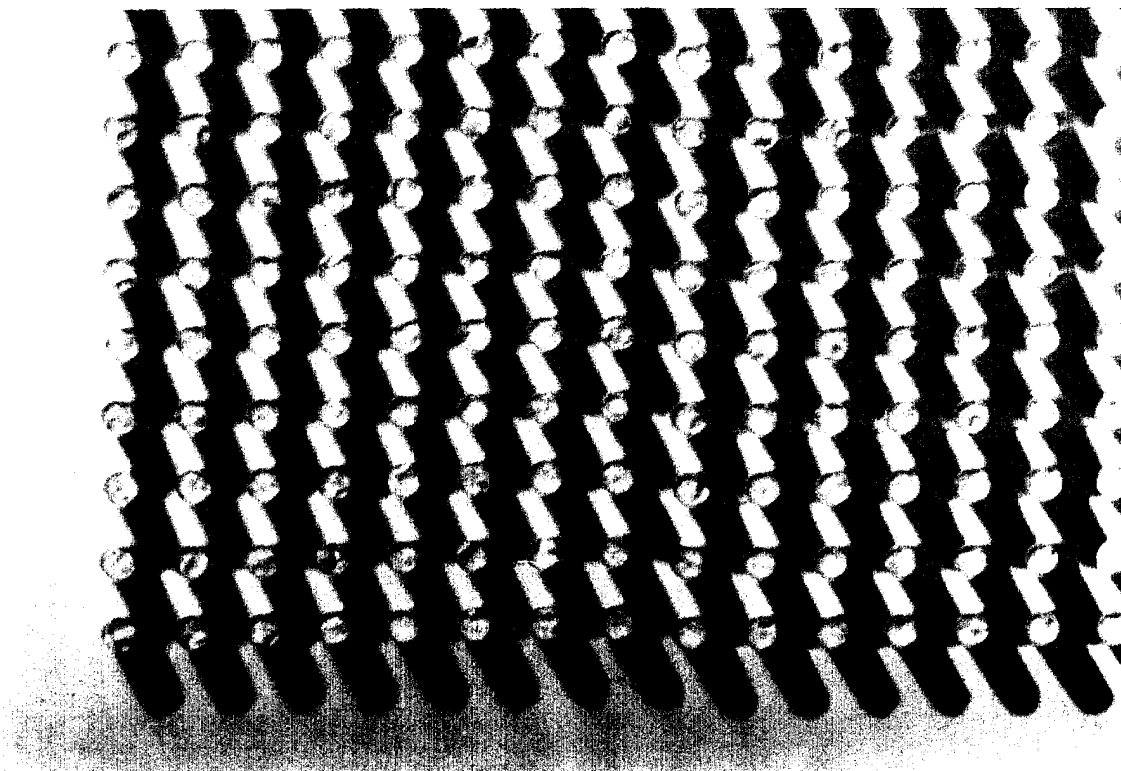


Figure 3: 1-3 composite PZT preform having $120\mu\text{m}$ diameter elements.

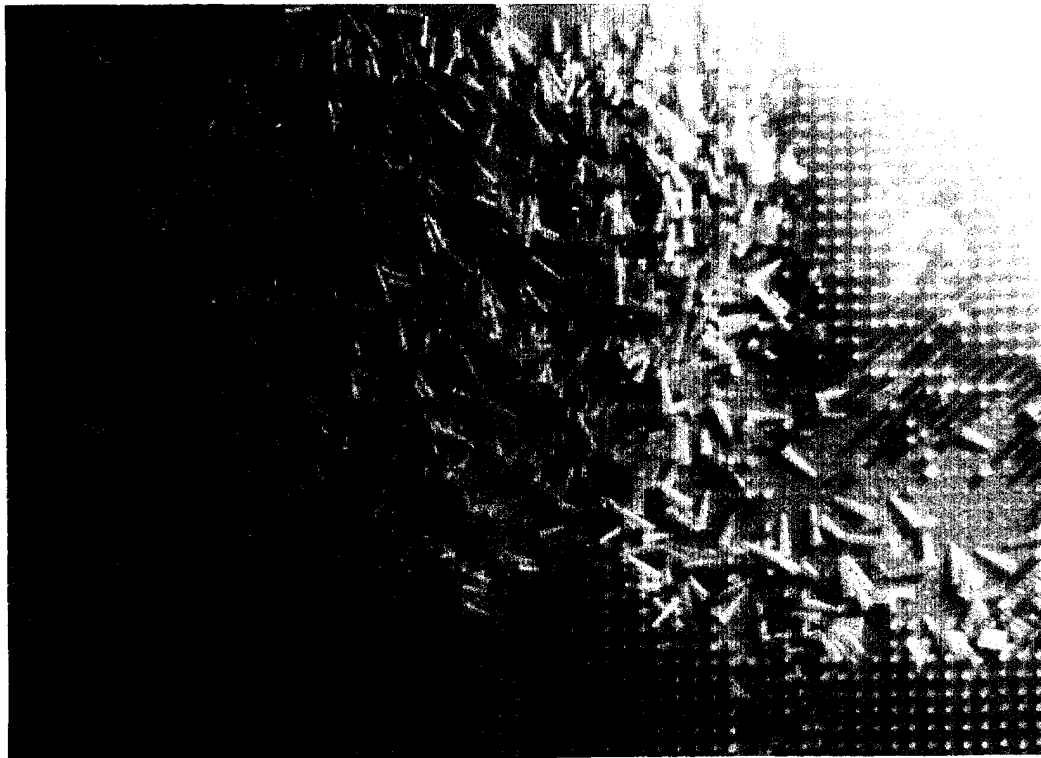


Figure 4: Aspect ratio of PZT rods in a similar composite to Figure 3.

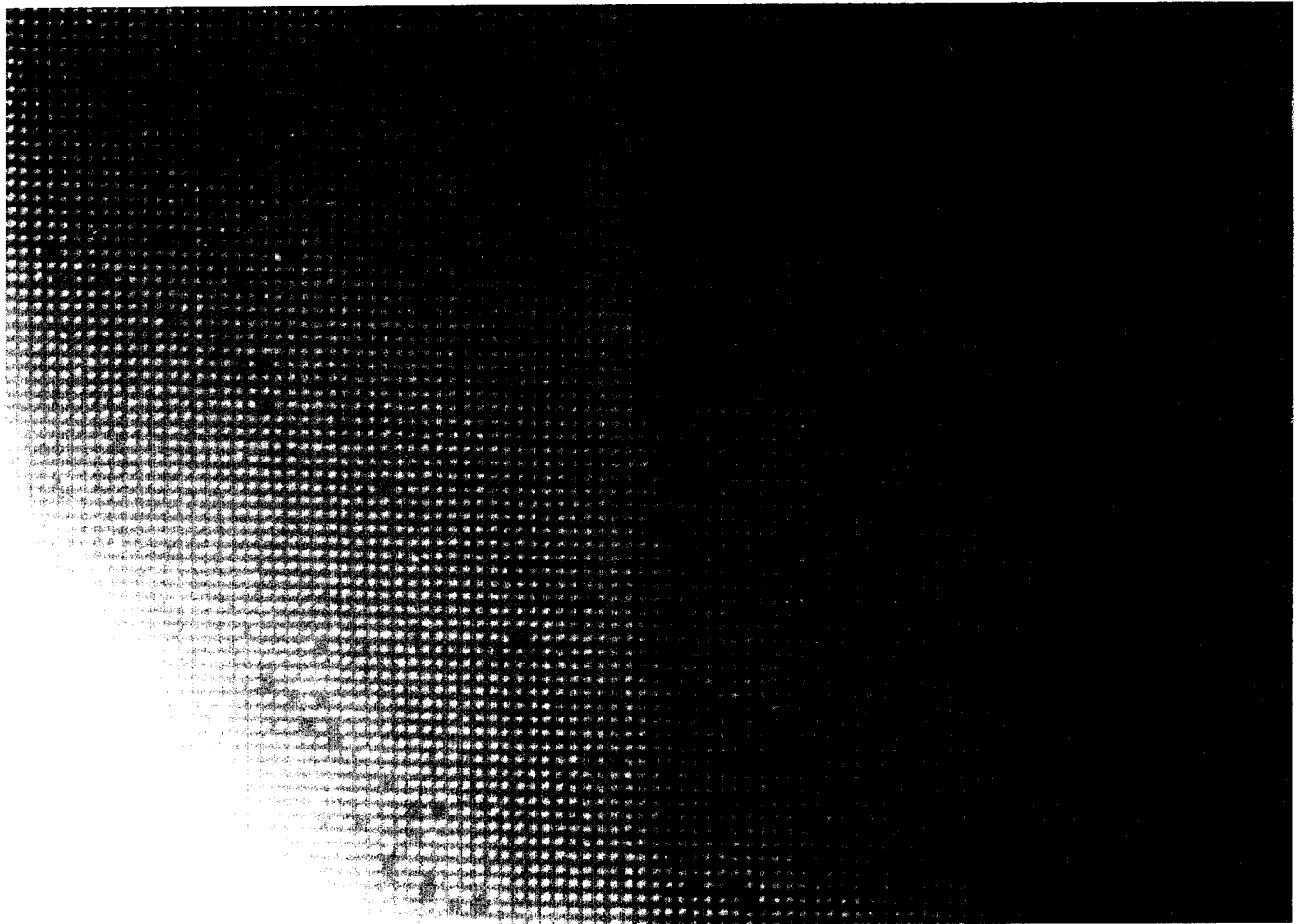


Figure 5: State-of-development 1-3 composite preform, 40 volume % PZT rods, 70 μ m diameter.

Over the past year, MSI received numerous requests from both Navy and commercial undersea imaging systems manufacturers for intermediate frequency 1-3 piezocomposites, operating in the 2-4MHz range. As a result of this near-term Navy interest, and after reviewing program priorities with the ONR Contract Monitor, MSI redirected its 1-3 composites effort onto materials having PZT element dimensions in the 200 to 400 μ m range. These 1-3 composite dimensions lie in a difficult process regime, not covered by any of the current MSI injection molding tooling approaches.

Several new tool fabrication options are being pursued for 2-4MHz transducers, aimed at both reducing tool cost and at achieving appropriate composite dimensions. As part of the tooling development activity, the tool application emphasis is focussed on improving the tool surface quality to facilitate molded part ejection.

Tooling cost is particularly important for large area 1-3 tools, high PZT content composites, and intermediate frequency piezocomposites (2-4MHz) that have >200 μ m diameter PZT elements. Recently, MSI has explored alternative tooling approaches, e.g. replacing hard steel with materials that can more readily be machined, and exploring new methods for making fine holes in the tool materials. These experiments have reduced the cost for research tooling by a factor of two, and have paved the way for further scaling up the composite area. MSI will continue these activities under an ongoing Phase II SBIR program that is aimed specifically at developing low cost tooling.

Fine Scale 2-2 Composites:

In the 2-2 composites area, MSI's research emphasis is driven by the need for high frequency 2-2 composites for intravascular and endoscopic imaging applications for both defense and commercial applications. These composites require ultrafine scale PZT element dimensions, i.e. pitches in the order of 35 to 100 μ m.

Using 2-2 tooling, MSI has achieved pitch dimensions as low as 45 μ m in 2-2 composites, lower than that reported by the dicing technique. Figure 6 shows a sample of a 50 volume % PZT preform manufactured by injection molding. The PZT features are approximately 22 μ m wide, and the individual PZT grains can be clearly seen in this SEM photograph. Several molding vestiges are evident on the as-fired surface, including traces of flash at the upper edges of the PZT strips where the tool inserts contact. There is no evidence that molding or sintering represent barriers to finer dimensions; rather, these are currently limited only by the binder removal process and the availability of suitable tooling. Pitches as low as 20 μ m appear feasible, but will require fresh tool insert fabrication approaches.

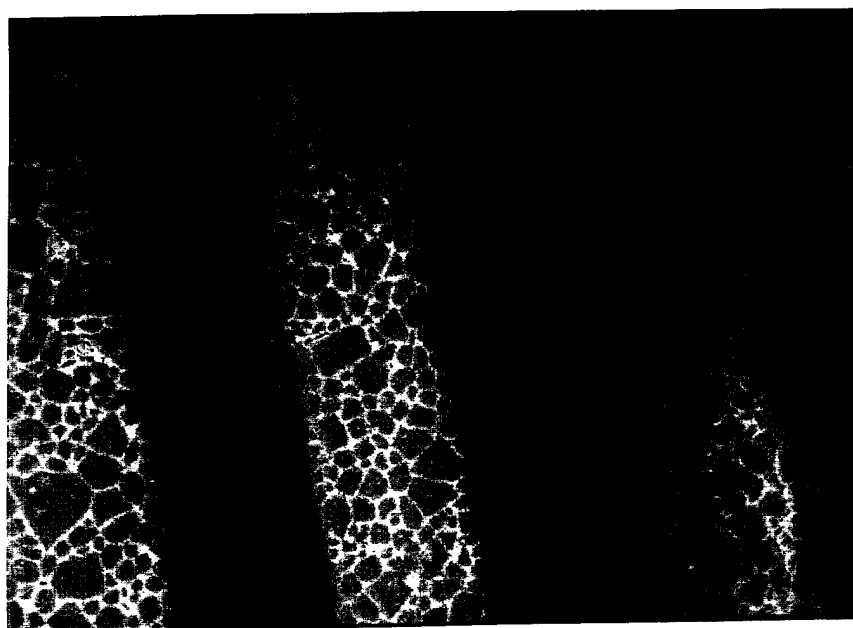


Figure 6: Scanning electron micrograph of as-sintered 2-2 composite preform having 45 μ m pitch at 50 volume % PZT content.

Binder Development:

The binder development activity has progressed according to schedule, with several new polymeric binders evaluated in the injection molding process. In the early work, these binder mixes had high viscosities and appeared unsuitable for use with the early fine scale tooling employed by MSI. However, new tooling options are now available that reopen the possibility of injection molding fine structures using high viscosity binders. These binders have several advantages over current wax-based binders in their burnout behavior, and are thus expected to find wide applicability in other MSI piezocomposite development and manufacturing activities.

Currently, these binders are being evaluated in terms of the strength of the as-molded green part, represented by increased yield of intact ejected PZT elements, and the ability to fill ultrafine dimensions. Dimensional stability during and after binder removal is being evaluated with respect to the sintered part dimensional tolerances.

Composite Characterization:

Impedance/frequency characterization of finished composites has been utilized to better understand the process and dimensional factors that influence lateral mode generation in MSI composites. Several methods for controlling lateral modes have been identified and explored, including modifying the polymer matrix, interelement spacing, element shape, and element dimensions. The injection molding process has greater flexibility for adjusting these parameters than alternative composite fabrication processes, such as dicing.

To prepare the composite samples for testing, techniques have been developed for incorporating polymer matrix materials into the sintered PZT preforms. For this purpose, MSI has chosen to use polyurethanes, leveraging experience gained in previous Navy contracts to apply this versatile family of materials to resonant composite transducers. These polymers add a new dimension to both undersea imaging and medical ultrasound transducer technology, which until now has mainly used epoxy resin for the composite matrix. Polyurethanes offer a wide range of stiffnesses, ranging from Shore A-(elastomeric) to Shore D-85 hardness, for exploring and controlling interelement modes.

Polyurethanes tend to be viscous and cure rapidly, therefore the early technical efforts focussed on developing methods for fully infiltrating the materials into the finest 2-2 groove dimensions. Lapping was attempted by outside vendors. After removing the baseplates on 2-2 samples, the lapped devices consistently delaminated at the ceramic/polymer interface, despite the use of gentle lapping procedures. This has been resolved by modifying the ceramic surface to improve adhesion, resulting in almost complete elimination of the delamination problem. Both 1-3 and 2-2 composites are now easily lapped. Chrome/gold electrodes with excellent adhesion have been applied to

samples for impedance/frequency characterization. Sputtered gold electrodes have also been used where long term adhesion is not important.

Lateral Mode Suppression:

Control of interelement spurious resonant modes is critical in both 2-2 and 1-3 piezocomposites. The problem arises when the PZT element dimensions and spacing are such that the thickness fundamental mode frequency coincides with the first and second lateral mode frequencies, which are determined by the polymer matrix properties and the nearest and next-nearest neighbor interelement spacing (2,3). The resonance spectrum then becomes a complex mixture of interfering modes.

Several options exist for controlling spurious modes in piezocomposites. These include:

1. Arranging the PZT elements in close proximity to each other so that the interelement mode frequencies are sufficiently above the thickness mode to prevent interference. This is the conventional method for interelement mode control used in medical ultrasound and undersea imaging. These composites usually require either high PZT volume fraction (and therefore possess high acoustic impedance), or extremely fine element dimensions.
2. Arranging the PZT elements to introduce interelement spacing variance. This prevents constructive interference by disrupting the array periodicity.
3. Varying the element shape to avoid adjacent facets which may promote cross-coupling between elements.
4. Adjust the polymer stiffness to reduce cross-coupling between elements. This is effective in suppressing interelement modes, but also adversely affects the thickness mode response by allowing the elements to move independently of the matrix.
5. Modifying the matrix to suppress cross-coupling, while maintaining the surface response uniformity, e.g. by incorporating additives into the polymer matrix phase.

The injection molding process facilitates these options by allowing variations in PZT element geometry and layout. Consequently, MSI has been exploring all of the above approaches under both program tracks.

Using modified tooling, MSI has succeeded in achieving very high PZT volume fraction in both 1-3 and 2-2 composites (Figure 7). In many cases this now exceeds 80 volume percent PZT. Some versatility in the ceramic element shape has also been demonstrated (Figure 8). The process requires further development, but offers considerable potential for producing 1-3 and 2-2 piezocomposites in which lateral modes are suppressed. These materials have not yet been fabricated into composites for evaluation of their electromechanical properties.

Using conventional injection molding tooling, MSI has pursued lower PZT volume fraction 1-3 composites (~25 volume % PZT) having various element shapes. For this composite layout, interelement modes become problematical when the PZT rod aspect ratio is between 2 and 3. This configuration is therefore an excellent choice for examining lateral mode effects, and has been adopted as the baseline for this work. Figure 9 shows this effect for a 0.5mm rod array fabricated under related contract number N00014-94-C-0019. Figure 10 shows the nearly ideal thickness mode resonance obtained for the SonoPanel configuration developed under contract N00014-92-C-0010 (3). In this case the PZT volume fraction is 0.3 and the rod dimensions are 1.1mm diameter by 6.3mm long (aspect ratio: ~5). The normal soft hydrophone polymer matrix and cover plates have been replaced with a hard (Shore D-80) matrix designed to facilitate uniform surface displacement. Lateral modes occur around 500kHz, well clear of the thickness dilatational mode. The composite configuration in Figure 11 is the same as in Figure 10 except that the material has been lapped thinner to increase the thickness resonance frequency to 1100kHz, resulting in rods of aspect ratio 1.5. Figure 12 shows the effect of a medium hardness matrix (Shore D-70) in controlling lateral modes. Although the composite element dimensions in Figure 12 are the same as those in Figure 10, spurious mode resonances are not detected. Since this material has a softer matrix than that of Figure 10, lateral mode responses are minimized, showing the importance of polymer matrix properties on interelement mode generation. The trade-off is that the surface response uniformity of soft matrix composites cannot be expected to equal that of harder matrix materials, which is a disadvantage in some applications.

Figure 13 shows an alternative design for diamond-shaped PZT elements, 0.64mm on a side, arranged in a regular array at 0.25 volume fraction. For this configuration, which cannot be made by dicing, there is no overlap of the faces on adjacent elements. However, at higher volume fractions, it can be seen that significant overlap occurs. This composite configuration was built under Contract number N00014-94-C-0019 and tested under the present program. The as-sintered rod array is shown in Figure 14. The matrix was a hard (Shore D-80) polyurethane. Figure 15 shows the impedance/frequency curve for this composite (aspect ratio: 2.5). Unfortunately, the interelement mode resonances are not reduced.

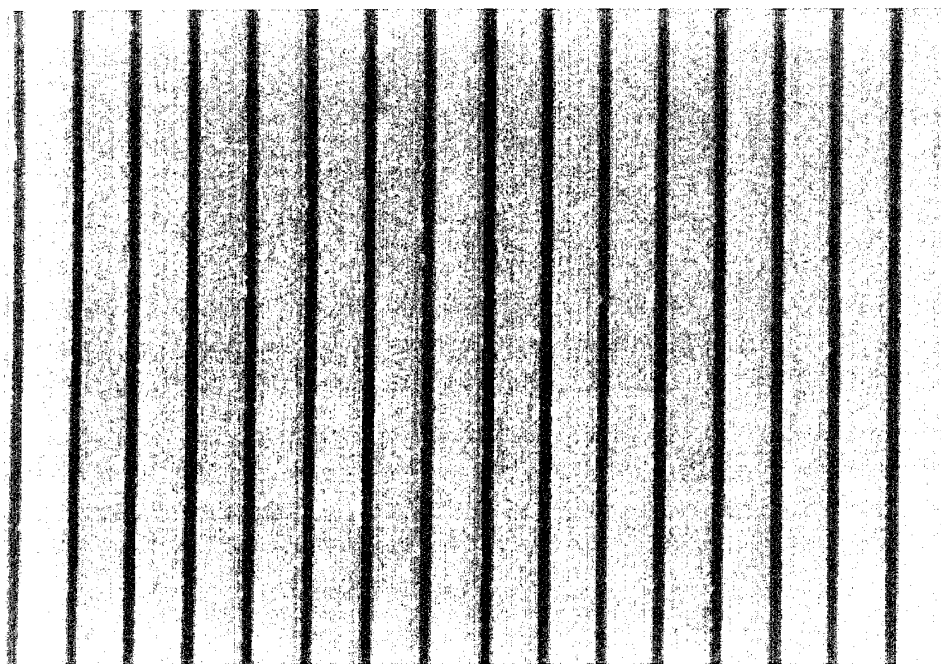


Figure 7: High volume fraction sintered 2-2 and 1-3 piezocomposite PZT preforms (pitch $\sim 150\mu\text{m}$).

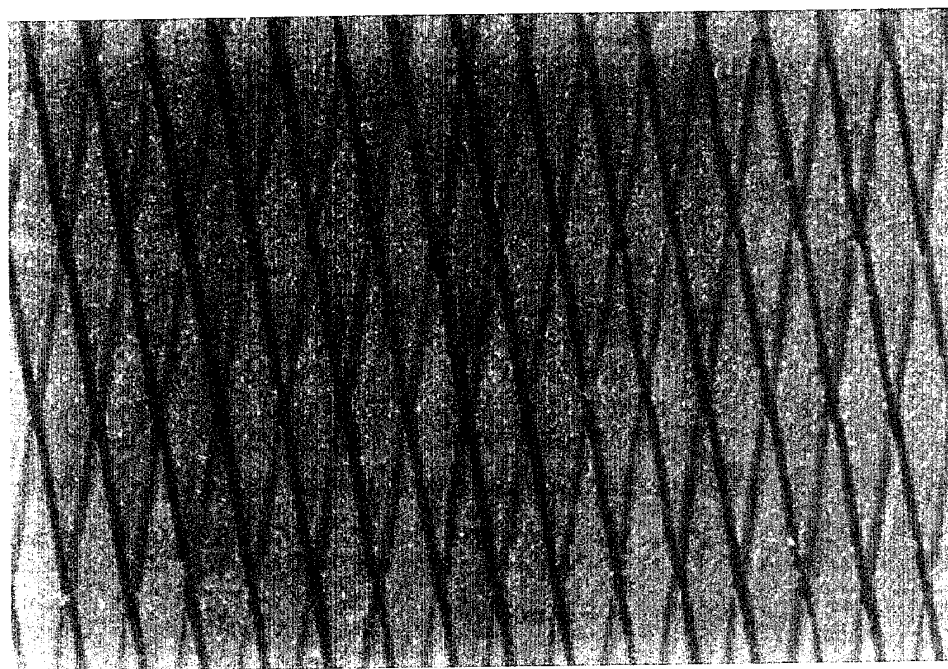
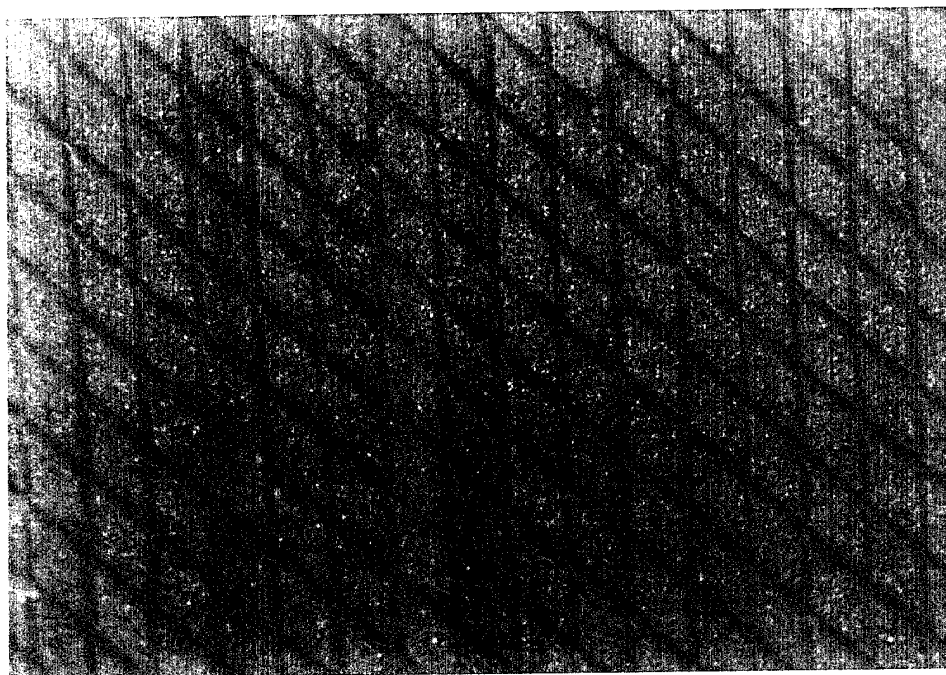


Figure 8: High PZT volume fraction 1-3 composites showing shape variability of the injection molding process.

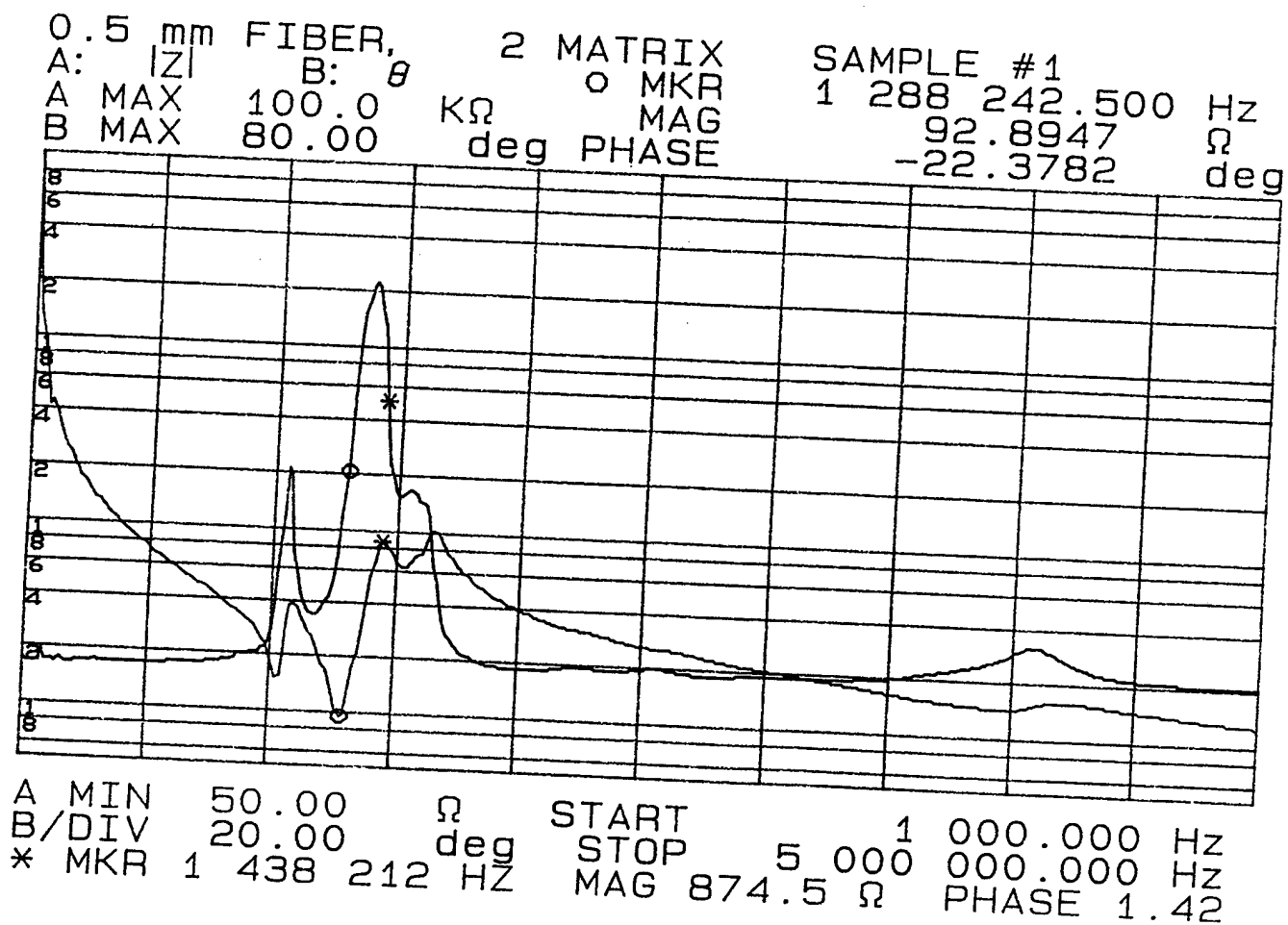


Figure 9: Impedance/frequency characteristics of 0.5mm diameter rod array, hard polyurethane matrix, 0.25 PZT volume fraction, PZT rod aspect ratio: 2.5.

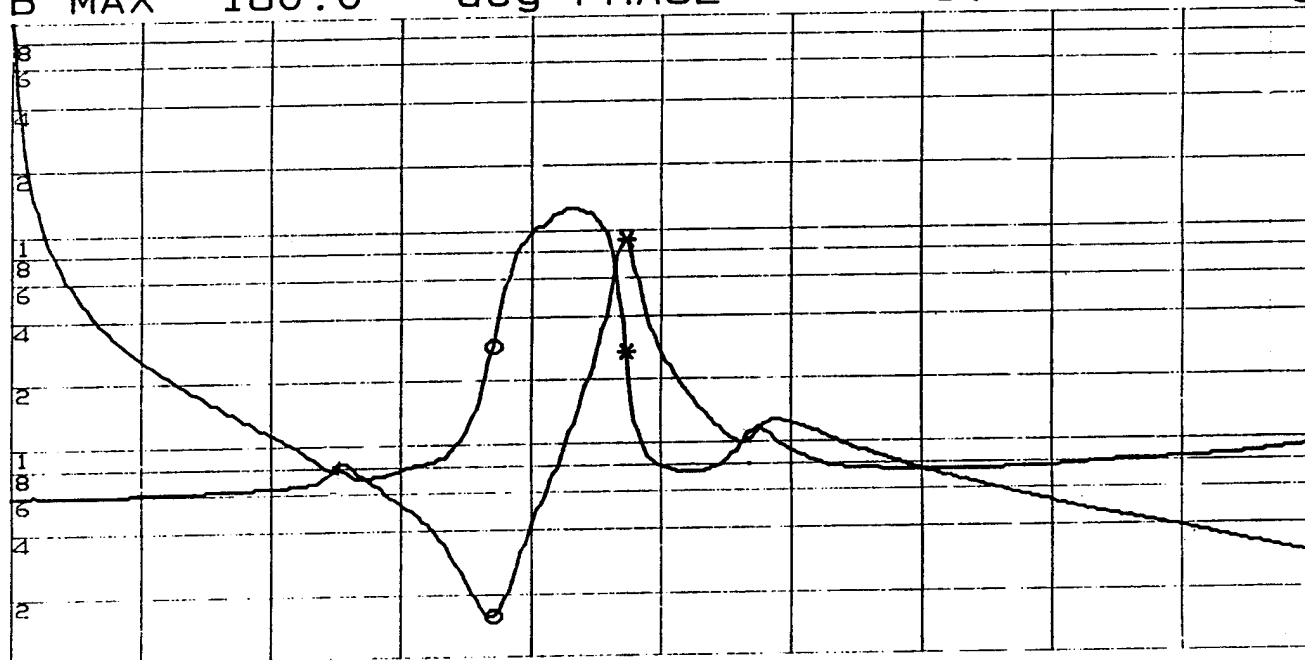
30% PZT HARD-8; 2 INCH DISK; TH = 0.250"
 A: |Z| B: θ o MKR 225 775.000 Hz
 A MAX 50.00 K Ω MAG 40.6749 Ω
 B MAX 100.0 deg PHASE 9.97961 deg



A MIN 10.00 Ω START 1 000.000 Hz
 B/DIV 20.00 deg STOP 1 000 000.000 Hz
 * MKR 280 720 HZ MAG 4.25 K Ω PHASE -5.03

Figure 10: Impedance/frequency characteristics of 1.1mm diameter rod array, hard polyurethane matrix, 0.30 PZT volume fraction, PZT rod aspect ratio: 5.

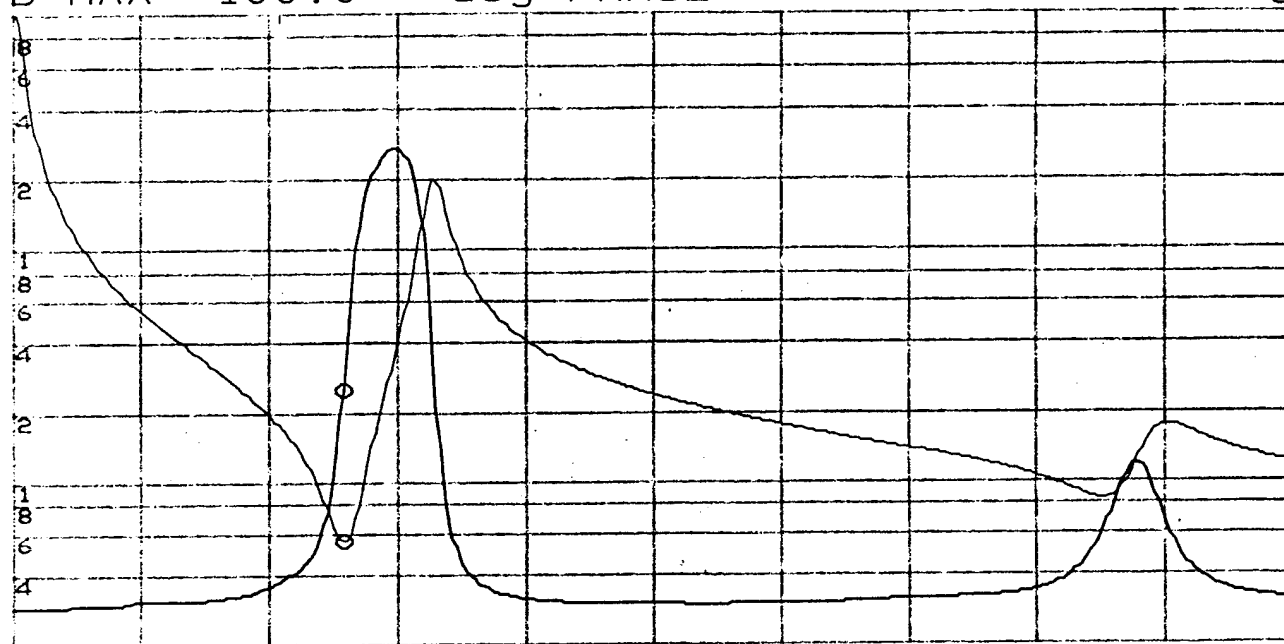
30% HARD MATRIX DISK DI= 2.75 TH= 0.048"
A: |Z| B: θ o MKR 1 110 630.000 Hz
A MAX 1.000 K Ω MAG 1.56617 Ω
B MAX 180.0 deg PHASE -3.82502 deg



A MIN 1.000 Ω START 1 000.000 Hz
B MIN -180.0 deg STOP 3 000 000.000 Hz
* MKR 1 418 027.5 Hz MAG 90.41 Ω PHASE -7.41

Figure 11: Impedance/frequency characteristics of 1.1mm diameter rod array, hard polyurethane matrix, 0.30 PZT volume fraction, PZT rod aspect ratio: 1.5.

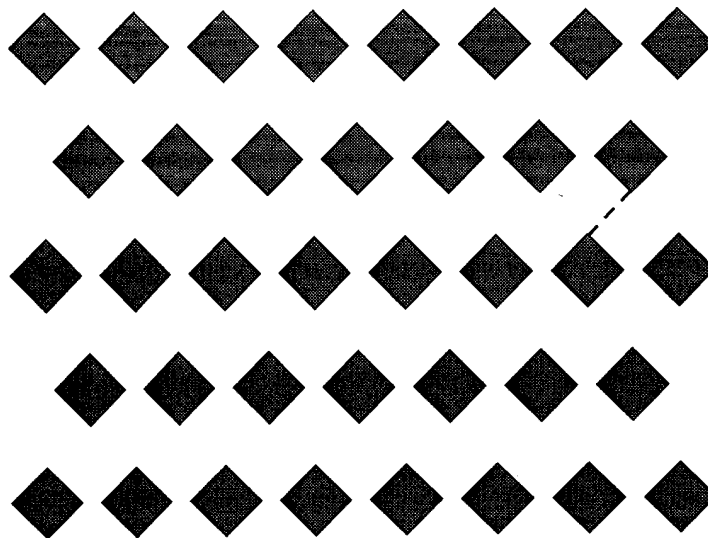
A: $|Z|$ B: θ o MKR 258 242.500 Hz
 A MAX 10.00 K Ω MAG 55.6812 Ω
 B MAX 100.0 deg PHASE -18.8662 deg



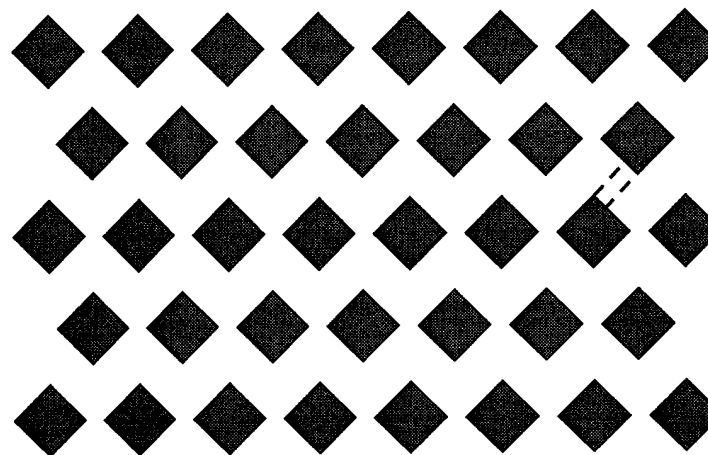
A MIN 20.00 Ω START 1 000.000 Hz
 B/DIV 20.00 deg STOP 1 000 000.000 Hz
 30% PZT THICKNESS= 0.250"

Figure 12: Impedance/frequency characteristics of 1.1mm diameter rod array, medium-hard polyurethane matrix, 0.30 PZT volume fraction, PZT rod aspect ratio: 5.

25.4 vol percent PZT



32.6 vol percent PZT



36.9 vol percent PZT

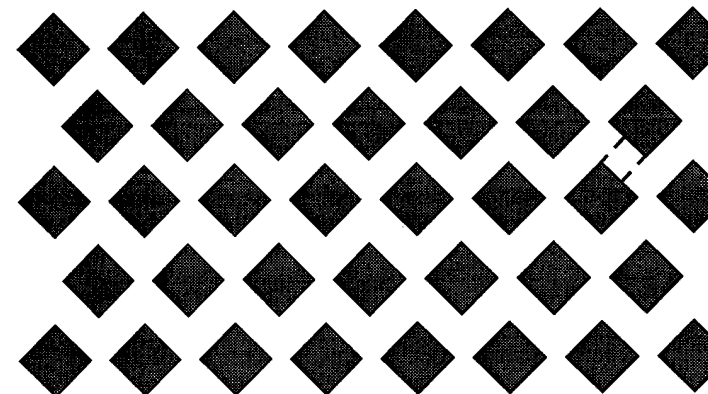


Figure 13: Design for a composite configuration with diamond-shaped elements for exploring interelement mode suppression.

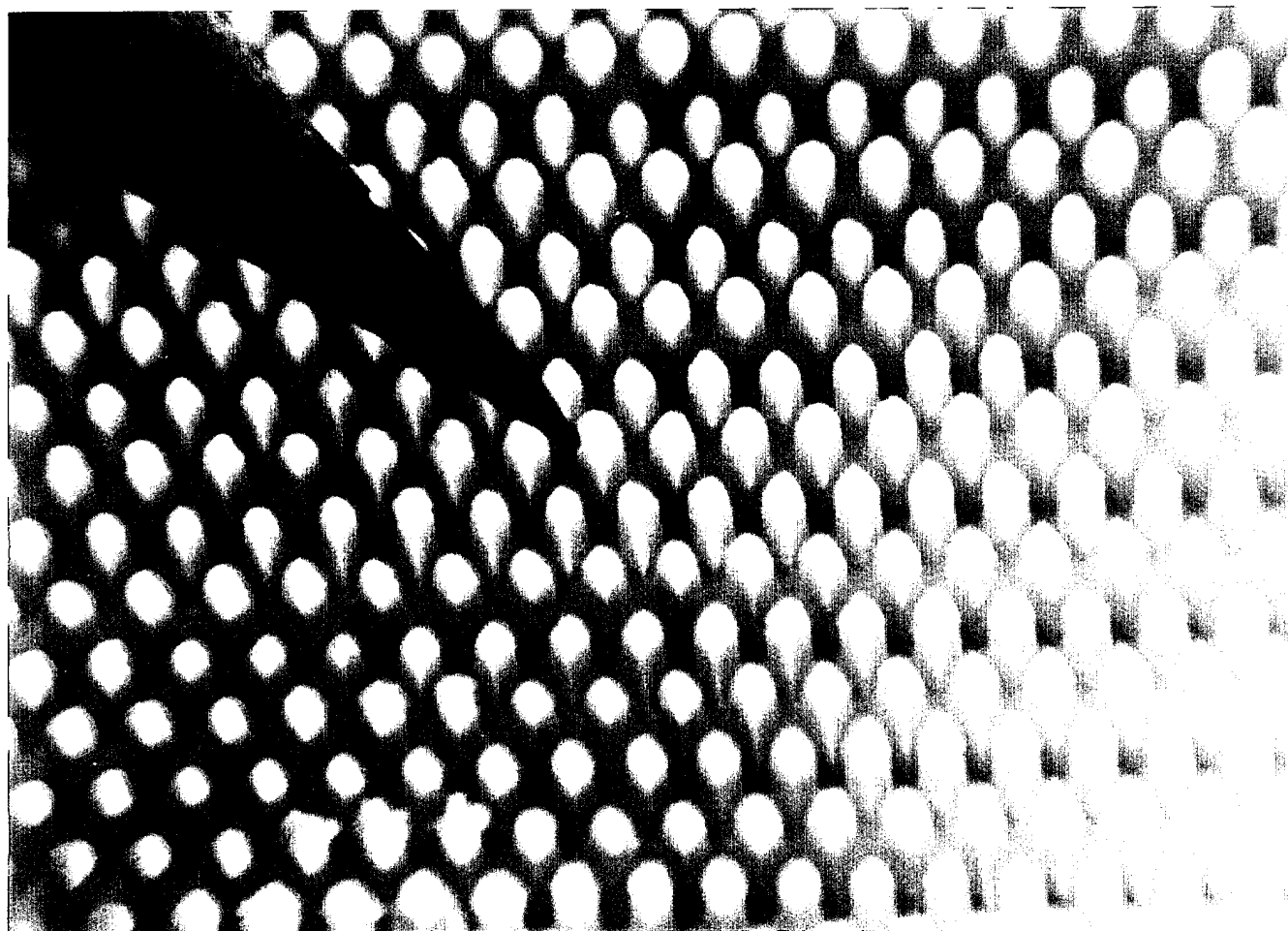


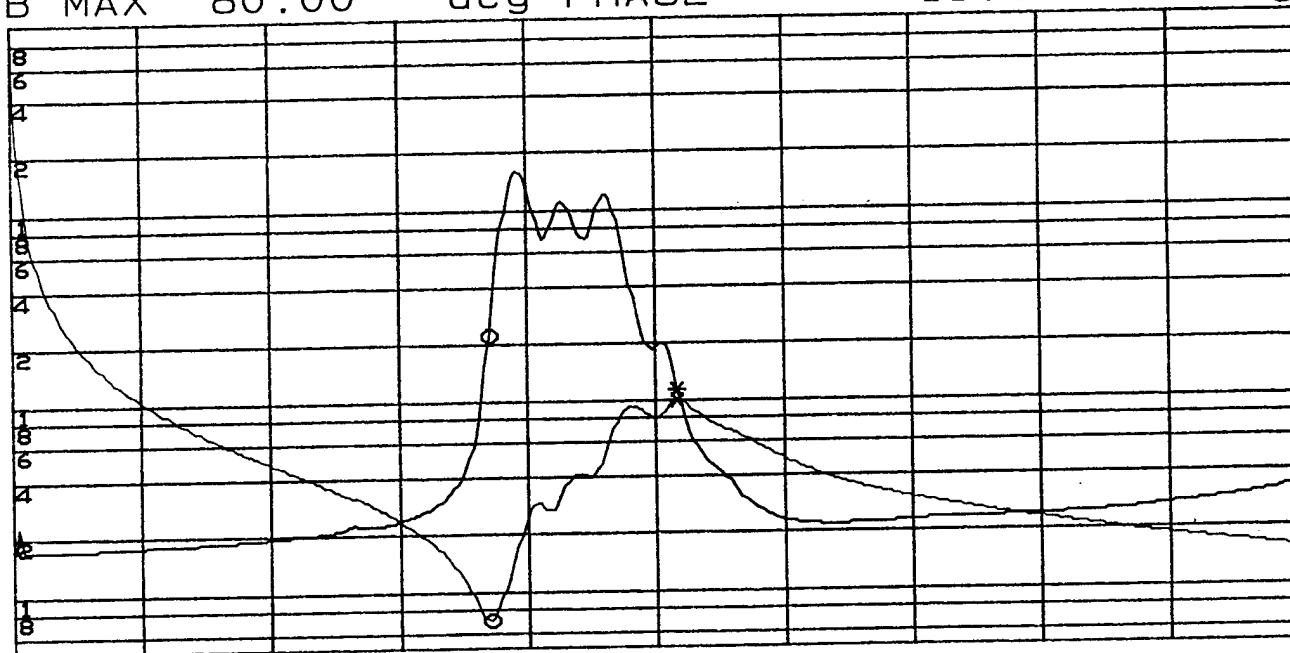
Figure 14: As-sintered PZT preform having diamond-shaped PZT elements.

0.64 mm DIAMOND FIBERS; HARD-8; TH = 0.050"

A: |Z| B: θ o MKR 1 110 630.000 Hz

A MAX 10.00 K Ω MAG 7.01003 Ω

B MAX 80.00 deg PHASE -19.9478 deg



A MIN 5.000 Ω START 1 000.000 Hz

B/DIV 20.00 deg STOP 3 000 000.000 Hz

* MKR 1 552 982 HZ MAG 100.3 Ω PHASE -38.18

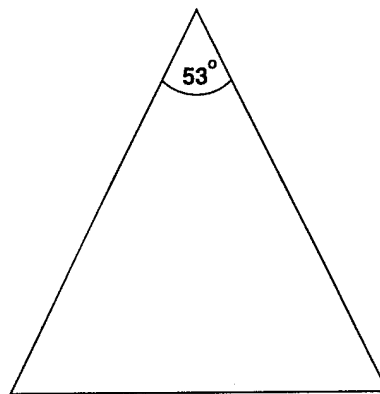
Figure 15: Impedance/frequency characteristics of 0.64mm square diamond-shaped rod array, hard polyurethane matrix, 0.25 PZT volume fraction, PZT rod aspect ratio: 2.5.

Further work was conducted on triangular-shaped elements designed by Strathclyde University under the TTCP portion of this program. The Strathclyde design is shown in Figure 16. In earlier work, Strathclyde had observed a significant reduction in interelement mode resonance with this PZT element configuration. However, the Strathclyde composite was assembled by hand-arranging diced triangular elements, resulting in natural variations in the element spacing which could account for the reduced interelement mode resonance. In the injection molded version, the element spacing is very uniform (Figures 17 and 18). Composites were made from the sintered preforms using four different polyurethane matrices: Elastomeric, Shore D-80, Shore D-85, and Shore D-80 with polymer microballoons. These were thinned by lapping to 3.25mm (2.5 rod aspect ratio), and tested for interelement modes.

Figures 19-22 show the resulting impedance/frequency plots. The elastomeric matrix appears to have an ideal resonance response because the polymer is so soft that the rods are completely decoupled and resonate independently from each other and the matrix. Essentially, this material is not functioning as a composite, but rather as an array of discrete piezoelectric ceramic resonators. For the harder matrices, interelement modes are plainly in evidence, even for the matrix containing microballoons. For periodic arrays of triangular elements, interelement modes have not been significantly reduced by the triangle shape or the presence of uniformly dispersed voids in the matrix.

It appears that PZT element shape modifications alone do not significantly reduce interelement modes in 1-3 composites. Varying the element layout may be a more promising lateral mode suppression technique. Significantly reducing the polymer matrix stiffness remains a viable route for lateral mode suppression, if this can be accomplished while simultaneously maintaining or even enhancing the thickness mode response uniformity. These options are being explored in the ongoing work.

Single element cross-section



25 volume percent PZT

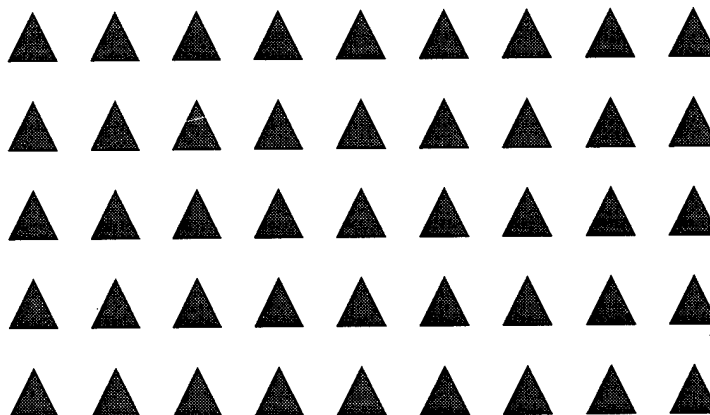


Figure 16: Strathclyde University piezocomposite design using triangular PZT pillars.

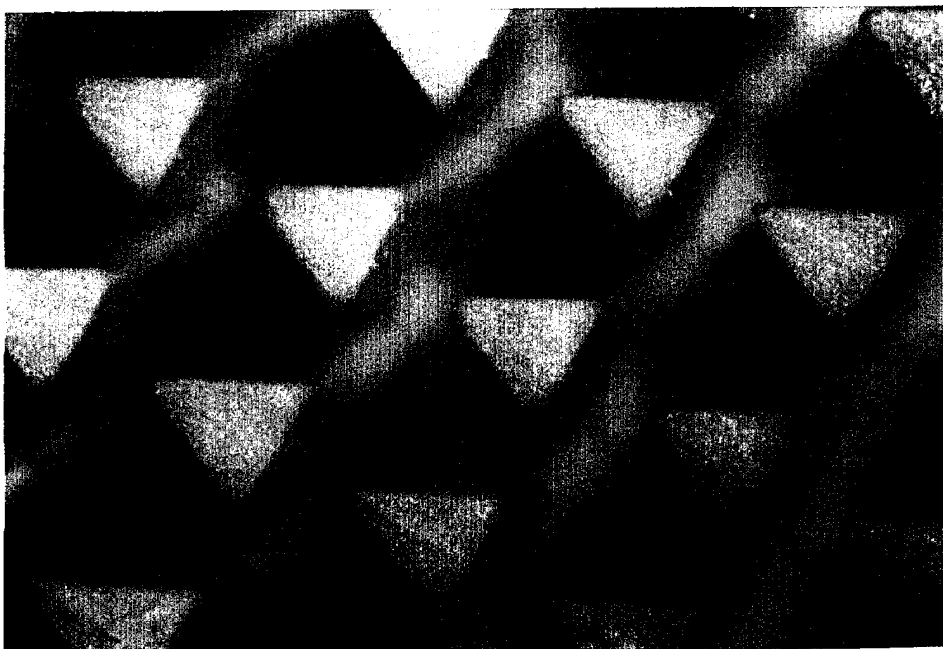


Figure 17: As-sintered array of triangular PZT pillars.

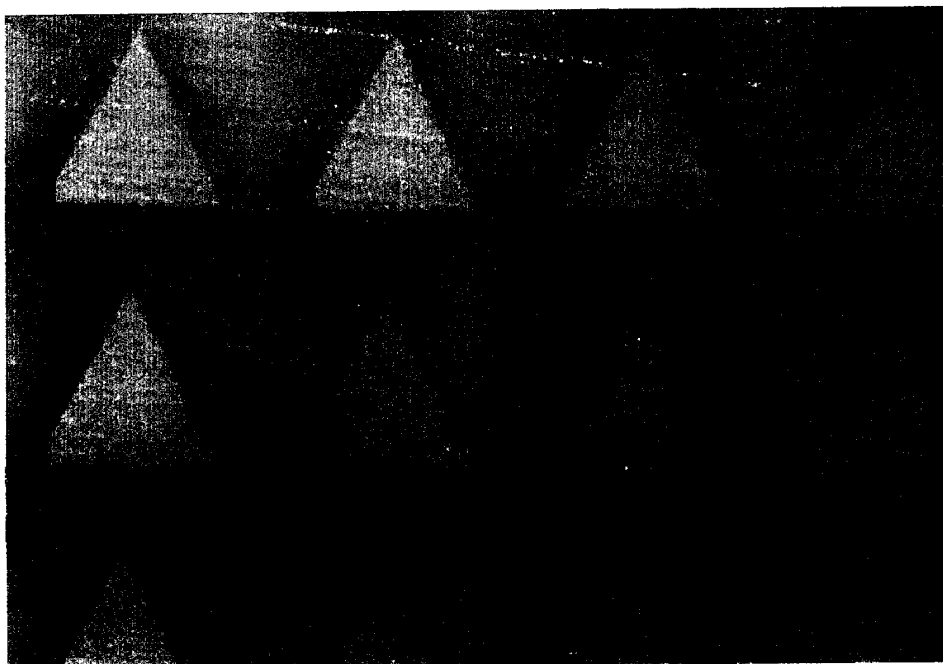


Figure 18: Triangular PZT pillars in Shore D-80 polyurethane matrix..

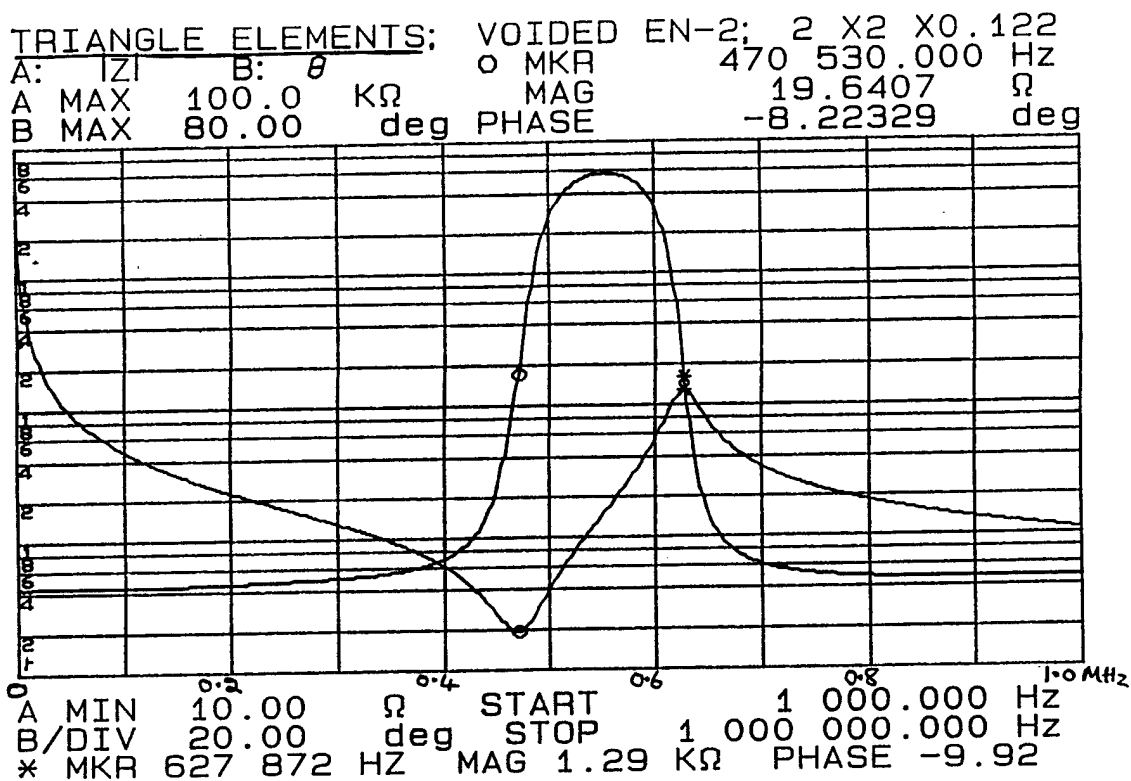


Figure 19: Impedance/frequency characteristics of triangular PZT element array, elastomeric polyurethane matrix.

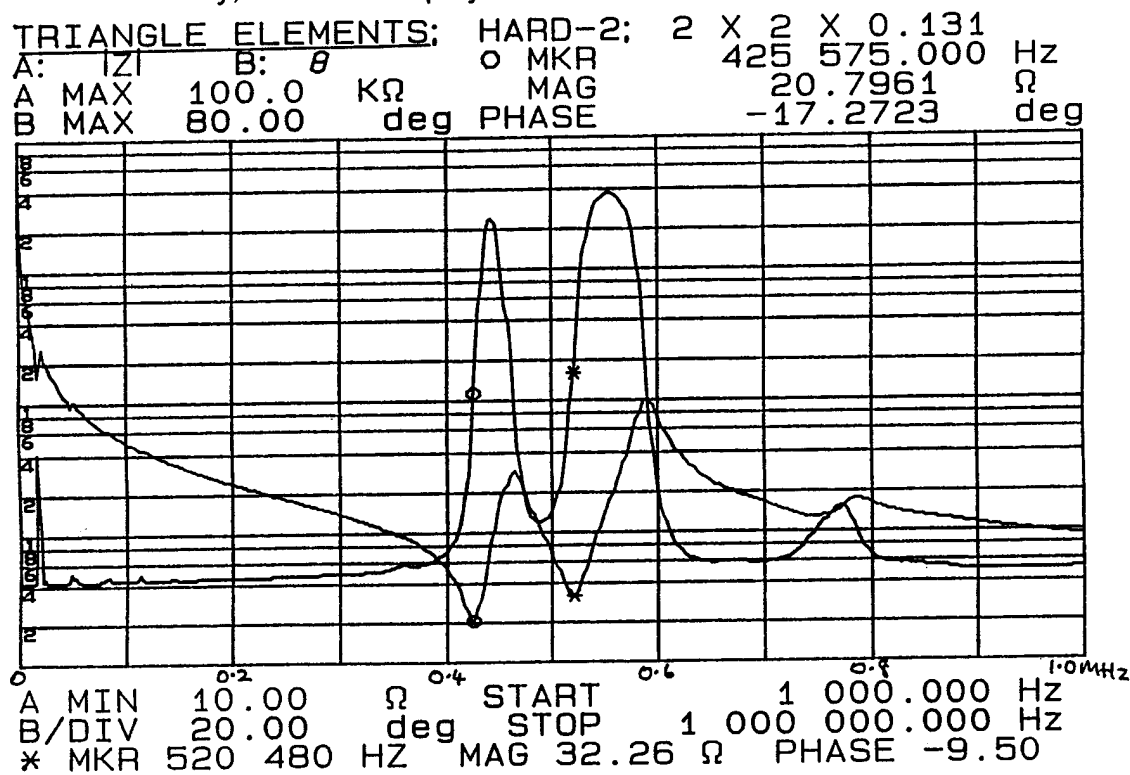


Figure 20: Impedance/frequency characteristics of triangular PZT element array, Shore D-85 polyurethane matrix.

TRIANGLE ELEMENTS: HARD-8; 2 X 2 X 0.131
 A: |Z| B: θ o MKR 400 600.000 Hz
 A MAX 100.0 K Ω MAG 21.5869 Ω
 B MAX 80.00 deg PHASE -31.6880 deg

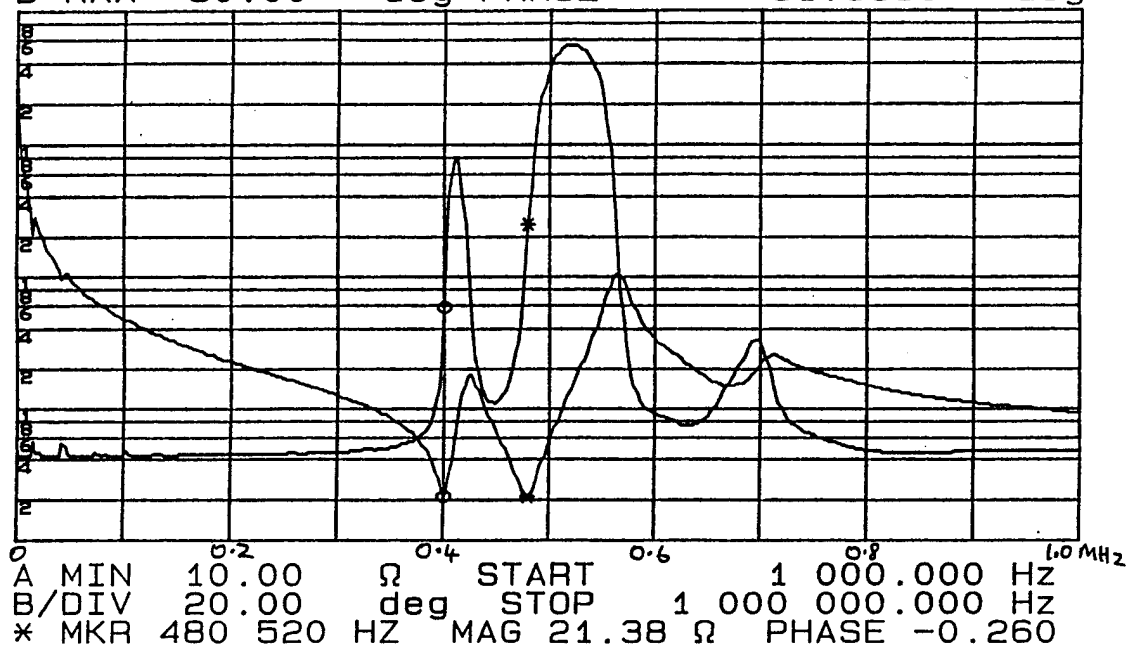


Figure 21: Impedance/frequency characteristics of triangular PZT element array, Shore D-80 solid polyurethane matrix.

TRIANGLE ELEMENTS: SOFT-8; 2 X 2 X 0.132
 A: |Z| B: θ o MKR 445 555.000 Hz
 A MAX 100.0 K Ω MAG 19.2115 Ω
 B MAX 80.00 deg PHASE -10.4337 deg

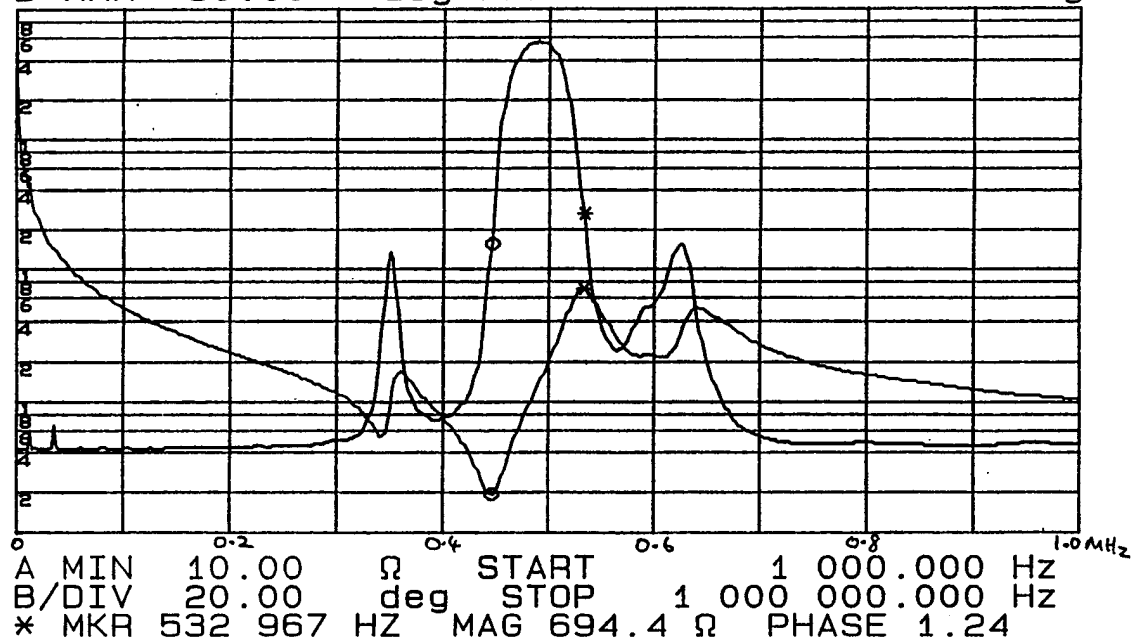


Figure 22: Impedance/frequency characteristics of triangular PZT element array, Shore D-80 polyurethane matrix with voids.

Track 2: TTCP Piezocomposites

In conjunction with other TTCP groups, MSI is participating in all three Technical Cooperation Program activities: Hydrophones, stacked transducers, and mine-hunting arrays. The TTCP participants are:

Canada:

Royal Military College (RMCC): Piezoelectric measurements.

UK:

Strathclyde University (SU): Piezoelectric composite modelling and design, testing.

Fugro-UDI (UDI): Undersea array design and testing.

DRA: Hydrophone testing.

USA:

NRL-USRD: Testing, input on US Navy needs.

Weidlinger Associates (WA),: Modelling.

UltraSound Solutions (USS): Undersea array design.

Materials Systems (MSI): Materials design and fabrication.

Hydrophones:

1-3 piezocomposite hydrophones are of considerable interest to the UK Navy for flank arrays, and therefore significant effort has been devoted to modelling, fabricating, and testing MSI SonoPanel configurations for this application. In the first six months of effort, MSI supplied two encapsulated 75mm SonoPanel transducers to DRA. These were RVS tested at low frequency (~50Hz) and found to have -185 dB re 1V/ μ Pa sensitivity, the same as that measured at 1-100 kHz on 100 and 250mm samples. Since then two more samples have been supplied to DRA for followup testing.

Strathclyde University has been performing modelling of hydrophones as part of their TTCP commitment. MSI supplied data and design parameters to both SU and WA over the past year for modelling purposes. The only data not available were the mechanical properties of the GRP cover plate materials. To circumvent the problem, MSI made a special 100mm SonoPanel transducer with aluminum cover plates that are more readily modelled. This device was sent to USRD for testing in mid-1994. Early results from USRD indicate that this

device has interesting resonance behavior; its bandwidth is significantly wider than that of GRP cover-plated devices.

USRD has devoted considerable effort to evaluating the resonance/frequency behavior of encapsulated SonoPanel transducers. A spurious resonance has been noted in unencapsulated devices at 100kHz, lower than the thickness dilatational mode (~220kHz) for the composite core material. Upon encapsulation, the spurious mode resonance frequency drops to about 70kHz when measured in air. When immersed in water, the 70 kHz mode shifts back to 100kHz, indicating that the encapsulation material is acoustically-transparent at this frequency, and the transducer resonates like an unencapsulated device. USRD and MSI are pursuing this with WA and SU in an attempt to better characterize the resonance mode and improve RVS and TVR performance uniformity. Details of the characterization work will be reported separately by USRD.

In related activity, MSI supplied samples of encapsulated and unencapsulated soft matrix composite transducers to RMCC for acoustic characterization. This has proved difficult due to the highly absorbing nature of the EN2 matrix, and characterization of this material has been discontinued. However, there is considerable interest in characterizing harder matrix composites, such as those described under Track 1. For this purpose, MSI is building a complete set of 1-3 composite samples having solid Shore D-80 matrix in the standard SonoPanel configuration for a complete characterization to IEEE Standards by RMCC. This is believed to be the first full tensor matrix determination for 1-3 piezocomposites.

Stacked Composites:

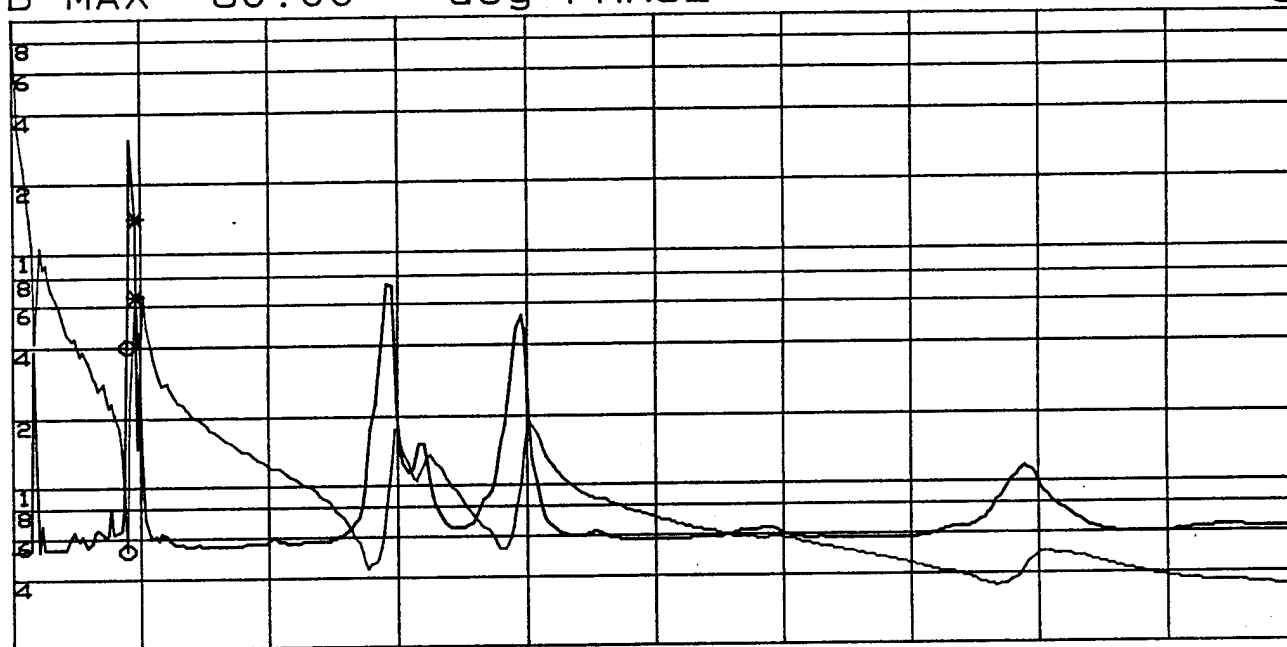
Under the TTCP, MSI made some stacked, unipolar piezocomposites having 15 volume % PZT in a hard polyurethane matrix, as well as two-layer devices having opposite polarity. Figure 23 shows data from a two-layer device having a single poling direction, driven across the total part thickness (12.6mm). The thickness fundamental mode occurs at 90kHz, as expected for a well-bonded composite. Figures 24 and 25 are impedance/frequency plots for a modified 1-3 composite in which the PZT baseplates have been left in place to mass-load the device and thus lower the thickness mode resonance frequency, which now occurs at 45kHz. In Figures 24 and 25 the resonance spectra are for two device types: A) poled and driven through the total thickness (unipolar); and B) poled in a back-to-back (multilayer) configuration, and driven between the center electrode and the two parallel-connected external electrodes. As these figures indicate, the impedance/frequency spectra for the two device types are very similar, showing that the multilayer configuration could function well as a low resonance frequency device at a fraction of the drive voltage required for a conventional thickness mode resonator.

Piezocomposites for Undersea Imaging:

This task is being accomplished in conjunction with Dr. Charles Desilets of Ultrasound Solutions, who is responsible for designing an undersea imaging piezocomposite array for mine-hunting applications. The key feature of this array is that the beam is steered electronically, rather than mechanically. At the beginning of the work, an array operating frequency of 500kHz was chosen to interface with an existing system under development by the British Navy. This requirement has set the basic 1-3 piezocomposite dimensional parameters, recently established in conjunction with UDI, USS, SU, and WA. MSI is now reviewing the composite parameters to establish the best tooling method for PZT preform manufacture. The composite differs from earlier ones made by MSI in that it requires 0.5mm elements on 0.75mm centers, which challenges the current tooling approaches.

The design for the undersea imaging array established by USS is described separately in Appendix 1.

15% PZT HARD-2 DOUBLE THICK
A: $|Z|$ B: θ o MKR 90 910.000 Hz
A MAX 100.0 K Ω MAG 521.900 Ω
B MAX 80.00 deg PHASE -23.7474 deg

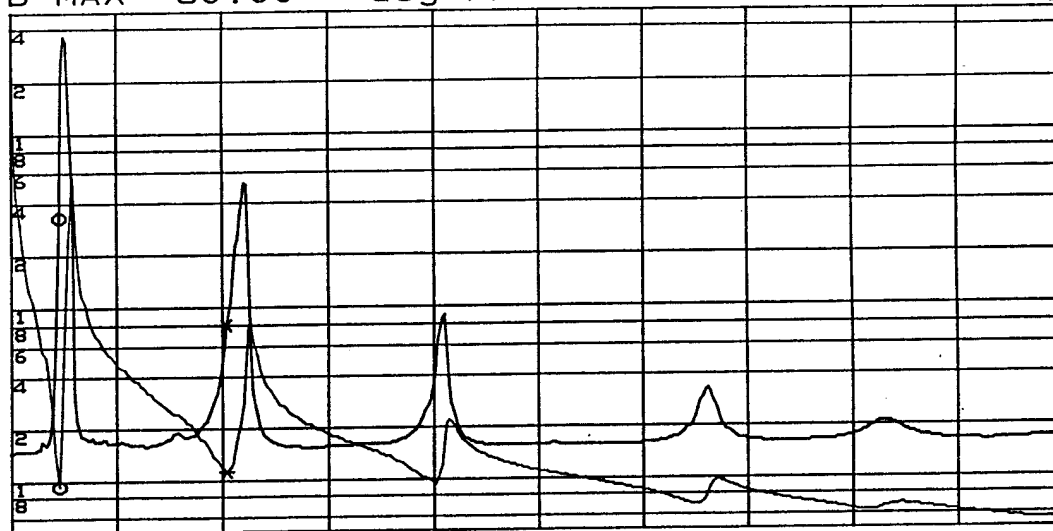


A MIN 200.0 Ω START 1 000.000 Hz
B/DIV 20.00 deg STOP 1 000 000.000 Hz
* MKR 95 905 HZ MAG 6.62 K Ω PHASE 17.55

Figure 23: Impedance/frequency characteristics of 1-3 double layer stacked piezocomposite in Shore D-85 polyurethane matrix.

15% PZT DOUBLE THICK;

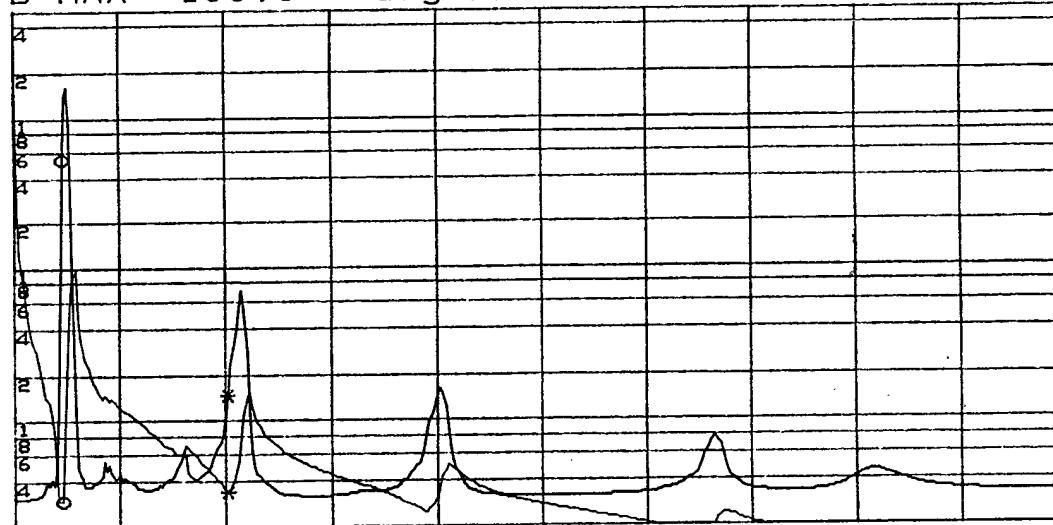
A: $|Z|$ B: θ o MKR 45 095.500 Hz
A MAX 500.0 K Ω MAG 936.156 Ω
B MAX 80.00 deg PHASE 1.51976 deg



A MIN 500.0 Ω START 100.000 Hz
B/DIV 20.00 deg STOP 1 000 000.000 Hz
* MKR 205 079 HZ MAG 1.13 K Ω PHASE -40.15

Figure 24: Impedance/frequency characteristics of unipolar, mass-loaded double layer 1-3 piezocomposite in hard polyurethane matrix.

A: $|Z|$ B: θ o MKR 45 095.500 Hz
A MAX 500.0 K Ω MAG 297.512 Ω
B MAX 100.0 deg PHASE 42.9036 deg



A MIN 200.0 Ω START 100.000 Hz
B/DIV 20.00 deg STOP 1 000 000.000 Hz
* MKR 202 579 HZ MAG 341.2 Ω PHASE -49.09

Figure 25: Impedance/frequency characteristics of multilayer, mass-loaded 1-3 piezocomposite in hard polyurethane matrix.

4. Summary

Materials Systems Inc. has demonstrated that net-shape ceramic injection molding is capable of fabricating extremely fine scale 1-3 and 2-2 piezoelectric ceramic/polymer composites for Navy and commercial applications. The injection molding capability has been extended to include ultrafine scale 2-2 composites having element widths as low as 22 μ m. The process and tooling have been refined to achieve larger area 1-3 composites, up to 30mm square. The past twelve months have seen 1-3 piezocomposites injection molded with high PZT volume fraction (~60-80%). Throughout 1993-94, MSI pursued commercialization of these materials, supplying test prototypes under customer funding to both private-sector and Navy composite end-users.

A major new initiative began in March 1994 into fine scale piezocomposites for undersea acoustic imaging. The applications drivers are Navy mine hunting systems and diver-held sonar. These materials are also expected to find application in the private sector, especially in medical ultrasound. This task continues as part of a Technical Cooperation Program (TTCP) in conjunction with other organizations in Canada, the UK, and the USA. MSI, in conjunction with UltraSound Solutions seeks to demonstrate that composite materials can be used for electronically beam-steered undersea acoustic imaging. A first generation transducer design for this application has been prepared by UltraSound Solutions for use in evaluating these materials.

Overall, the program goals in both the ultrafine scale composites and TTCP activities have been met on schedule and within budget. Feedback on applications from Navy and commercial systems end-users has prompted MSI to perform additional exploratory demonstrations of its process for transducers that operate in the 2-4 MHz frequency range. Navy and medical ultrasound interest in this frequency range remains strong, and has been factored into MSI's recommendations to ONR for continuation of this work during 1995-96.

5. References

- 1) "Near Net-shape Fabrication of Ultrafine Scale Piezoelectric Ceramic/Polymer Composites", ONR Contract Number N00014-92-C-0212: Annual report, Sept. 1993 .
- 2) "Cost-effective Method for Synthesizing innovative Transducer Materials for Sensors and Actuators", Final Report ONR Contract Number N00014-94-C-0019, June 1994.
- 3) "Fabrication of Piezoelectric Ceramic/Polymer Composites by Injection Molding" Final Report ONR Contract Number N00014-92-C-0010, April 1993.

Appendix 1: UltraSound Solutions Annual Report

UltraSound Solutions
1215 Highland Drive
Edmonds, WA 98020

Underwater MCM Arrays Using Composite Piezoelectrics

PROGRESS REPORT

February, 1994 - February, 1995

A review of undersea imaging applications was conducted by C. Desilets (UltraSound Solutions) with the assistance of C. MacLean (UDI-Wimpol) to determine the range of potential uses for electronically scanned imaging systems and the applicability, if any, of technology developed for the medical ultrasound industry. The review was conducted to determine the basic imaging system performance parameters required to meet the requirements of detection, classification, and identifications of underwater objects. From these basic parameters, the specific requirements for transducer arrays to support several new undersea imaging systems was to be developed. These requirements in turn will determine the requirements for fine-scale piezoelectric composites to support these arrays.

The review has focused on the Fugro-UDI Sonavision 4000, various side-scanning sonar systems, and the University of Washington APL acoustic lens system. These systems were studied, and preliminary results for the employment of electronically scanned arrays in these systems were presented at the TTCP meeting in September, 1994. A comparison of medical versus undersea imaging is shown in Table I. Of particular note, the long range required in undersea imaging generally requires imaging in the far-field. The resolution is solely determined by the aperture of the transducer antenna and the frequency of operation. The long propagation time resulting from the long operational range precludes using multiple transmit pulses as done in medical imaging. This results in high intensity transmitter arrays which insonify the whole field of interest at one time as opposed to the highly focused transmitter beams used in medical imaging. As a result, separate transmitter and receiver arrays are often used in underwater imaging. The scanning formats are quite similar, however, in that linear, curved, and phased arrays are used in both areas; and beamforming issues like grating lobes, sidelobes, and apodization are common to both modalities. For transducer design, the key difference is that the transmitter and receiver arrays in underwater imaging can be separately optimized and should result in quite different materials and microstructure for the arrays.

The MCM array development team was formed at the September TTCP meeting at Holton Heath, UK for the purpose of developing advanced array designs for MCM. Team tasks include identifying a practical MCM application which would benefit from advanced composite arrays, designing array(s) to meet that application, simulating the design of these arrays using an advanced time-domain finite element code developed by Weidlinger Associates, developing composite materials and array structures to improve array performance parameters, and building and testing feasibility array structures and prototype arrays. Team members include C. Desilets, UltraSound Solutions (project lead), C. MacLean and V. Murray, UDI-Wimpol (system design and test), G. Hayward and J. Bennett, University of Strathclyde (composite design and array simulation), G.

Wojcik, Weidlinger Associates (simulation tool development), L. Bowen, Materials Systems (composite and array fabrication), and B. Mukherjee and S. Sherrit, Royal Military College (materials characterization).

During the past report period, C. MacLean identified a Defense Research Agency MCM application that could benefit from advanced ultrasonic array designs. Top-level system specifications were transmitted to the team for review in late October, 1994. A trade study was performed by C. Desilets on various solutions suggested by C. MacLean for arrays that would meet the system requirements for a minimum 90° scan sector and a minimum number of channels. These included a curved transmitter array and a phased linear array receiver to address the 90° scan sector, a pair of phased receiver arrays crossed at a 45° angle to compensate for an expected element acceptance angle of less than $\pm 45^\circ$, and a curved array design requiring no beam steering. The curved array solution was adopted as the primary vehicle for composite material and array development since it places less stringent requirements on the element acceptance angle. A preliminary design of a 105 element, 150° aperture, and 120 mm radius curved receiver array was presented.

The curved receiver array design parameters were established by first allowing the size of the array to increase from the initial 160 mm envelope to 235 mm. This still appears to fit inside the present MCM vehicle head while necessitating the removal of some ballast material. This design change still needs to be confirmed as allowable. A 120 mm aperture yields the requirement for a 1.5° beam, as shown in Figure 1. Assuming that the maximum acceptance angle that can be obtained in an array of one wavelength pitch is $\pm 30^\circ$, the minimum radius of a curved array with a 120 mm aperture is 120 mm, the requirement stated above and shown in Figure 2. To achieve a 90° sector using a full 120 mm aperture over the entire sector means using a 150° curved array. The length of this array is 314 mm which yields 105 elements on a 3 mm pitch. With this pitch, the scan lines will be separated by 1.5° as well, matching the beam width parameter quite nicely. The elevational aperture is 11.5 mm yielding the desired 15° vertical beamwidth as shown in Figure 3. The length of this 150° , 120 mm radius curved array projected onto the azimuthal axis is 232 mm, as required. The main issue with the use of this curved array will be achieving the theoretical 30° acceptance angle in a composite array structure. This point will be the focus of research during the next several months.

G. Hayward reported on the progress made with finite element simulations and verified in part by laser interferometry by J. Bennett at the University of Strathclyde using both ANSYS and the Weidlinger Associates PZFlex codes. Simulations have shown the criticality of pillar aspect ratio to various transducer figures of merit, the sensitivity of dilation quality of an array element to pillar aspect ratio, the effect of polymer stiffness on dilation quality, and the importance of having excellent measurements of polymer damping in both longitudinal and shear modes. Several rules of thumb for composite array design have been developed and will be verified over the next months as part of this program. A most critical feature for array design was the addition to PZFlex of the simulation of the far-field beam pattern using the pressure and displacement distribution at the surface of the array element with the Fourier transform algorithms. Some verification of the technique was demonstrated by simulating the pattern of an ideal piston radiator. Since array design is dictated by the achievable angular beam distribution in a given structure, having a simulation capability based on real, not idealized, transducer structures is a major advance in the state of the art.

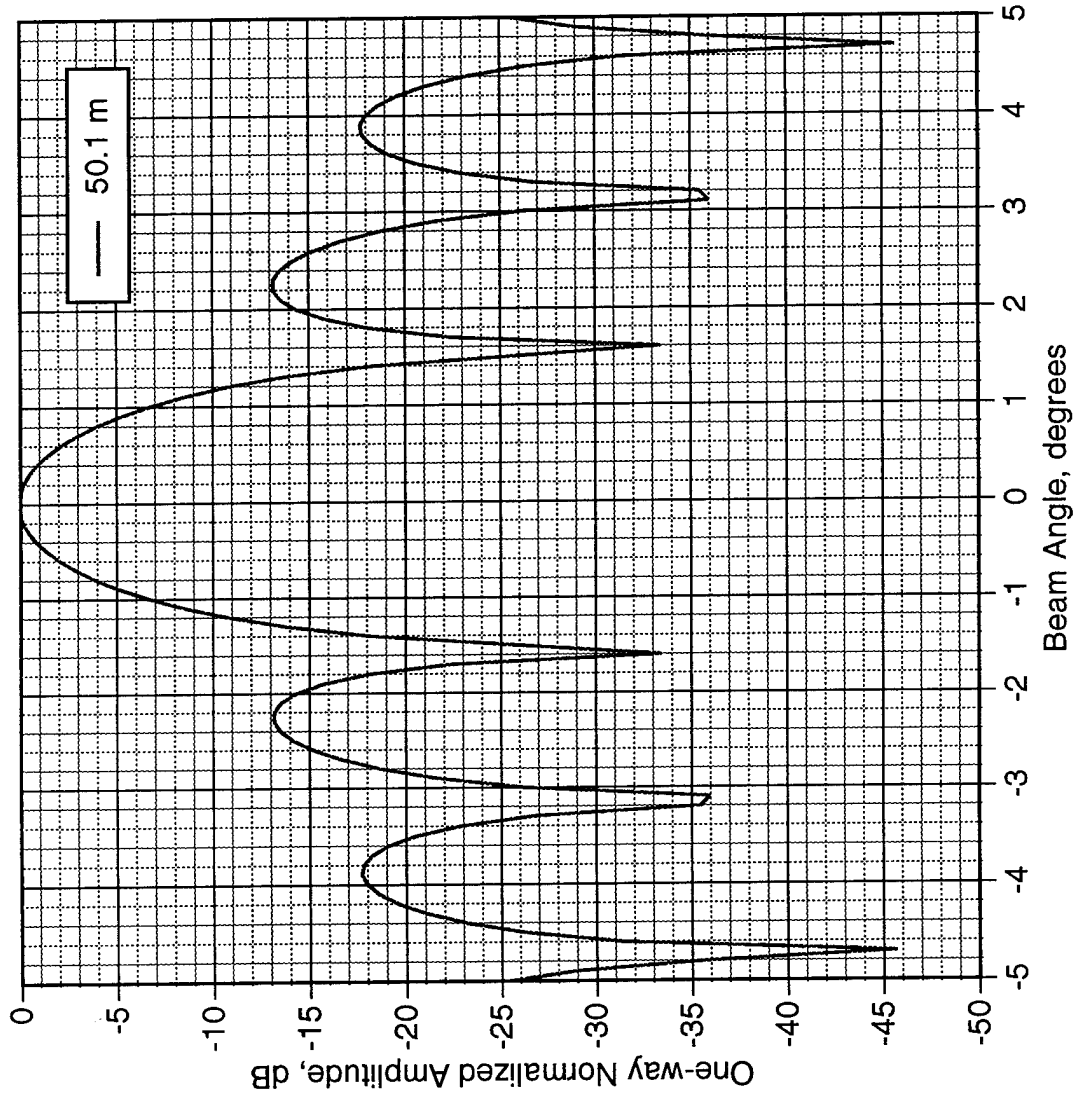
Progress was reported by L. Bowen on the manufacture of 1-3 composites based on a triangular pillar shape intended to reduce cross-coupling as designed by Strathclyde. New low-cost tooling is being used to construct the material and should be ready in late March. S. Sherrit reported on the measurements of 1-3 composites manufactured by MSI with hard polyurethane polymer. He agreed to attempt to find the resources to measure the properties, especially loss, of polymer filler materials under consideration. G. Wojcik reported on various modeling activities conducted by Weidlinger Associates using PZFlex.

In the next report period, C. Desilets and C. MacLean will finalize the design of the curved receive array and develop the specifications for the final prototypes; C. Desilets will develop several array designs using Strathclyde's new design rules of thumb and L. Bowen will construct feasibility mini-arrays using these designs for test by UDI and Strathclyde; J. Bennett will continue his modeling and verification effort with PZFlex on array structures; S. Sherrit will provide materials characterization support; and G. Wojcik will provide modeling enhancement support.

TABLE I
COMPARISON OF UNDERSEA TO MEDICAL IMAGING

| PARAMETER | UNDERSEA IMAGING | MEDICAL IMAGING |
|---------------------------------------|---|---|
| Range | 3 meters to 100 meter | 2 to 20 centimeters |
| Echo Arrival | 13.3 milliseconds | 26.7 microseconds |
| Transmit Pulses | Many receive lines per pulse | Several pulses per receive line |
| Resolution | Low resolution, far-field imaging | High resolution, focused, near-field imaging |
| Frame rate | Non-real time | Real time (15-30 frames/second) |
| Target Characteristics | High reflectivity, specular | Low reflectivity, scattering |
| Target Density | Sparse | Rich |
| Target Interest | Surface profile detail | Interior detail |
| Dynamic range | 80-100dB | 120-140 dB |
| Lateral Resolution | Unfocused with resolution set by aperture width | Highly focused in one plane with up to f/2 apertures |
| Resolution - Effect of Transmit Pulse | Reduced by the necessity for wide transmit beams | Matched transmit and receive apertures for enhanced resolution |
| Transmit Power | Limited by cavitation | Limited by regulation |
| Axial resolution | Moderate, reduced by narrowband, long (20 cycles) pulses to increase average power, hence range | Fine, enhanced by wideband, short (2.5 cycle) pulses for excellent axial resolution |
| Signal Processing | Extensive to improve SNR | Virtually none |
| Frequency range | 150 kHz to 3 MHz | 2 to 10 MHz |
| Elevation Aperture | Diverging fan beam | Weakly focused beam |
| Imaging Format | Slant angle insonification separates targets in range | Focused beam yields tomographic slice |
| Two-dimensional Arrays | Low element count, fully dense or Mills Cross arrays | 1.5 and 2D arrays in development |
| Operational Modes | Detection, classification, and identification | Identification only |
| Transmission and Reception | Separate transmitter and receiver arrays | One array for both transmission and reception |
| Beam steering | Phased and curved arrays both used | Phased and curved arrays both used with fine delay focusing |
| Transducers | Narrowband transmitter and receiver independently optimized | Wideband transmitter and receiver optimized together |

Figure 1: Beam width of a 120 mm Aperture at 500kHz



**Figure 2: Geometry of 500kHz, 120 mm radius,
150 degree Curved Array**

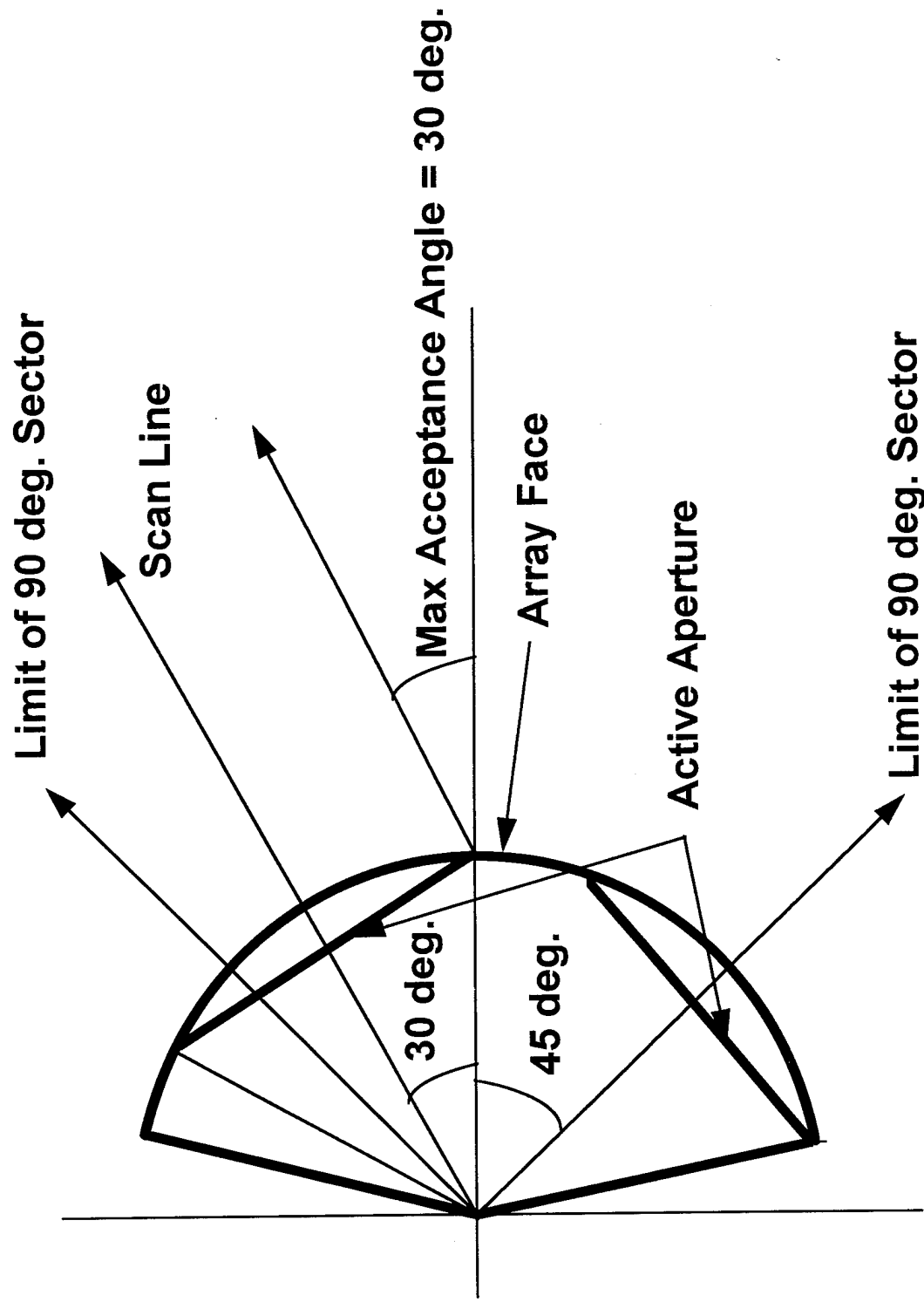


Figure 3: Beamwidth of a 11.5 mm Aperture at 500kHz

